INFORMATION THERMODYNAMICS

Measuring how effectively light drives a molecular pump

Information thermodynamics offers a route to measure how effectively a light-driven molecular machine converts energy from absorbed photons into pumped motion.

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Thermodynamics was developed to analyse the performance of machines that transduce heat into work. Central to that endeavour was the derivation of the Carnot efficiency, the maximum theoretical efficiency of such an interconversion. Since the time of Carnot, artificial machines have moved from the macroscopic — heat engines and refrigerators — to the microscopic, led by both experimental and theoretical advances. Writing in *Nature Nanotechnology*, Corrà, Tranfić Bakić and co-workers bring together these experimental and theoretical advances to quantify how efficiently a molecular machine transduces energy from one form into another[1].

On the experimental side, the authors synthesize a well-studied pseudorotaxane supramolecular system consisting of a macrocylic ring that threads onto and off an axle[2,3]. That axle can in turn interconvert between a straight and a kinked configuration through a photo-isomerization reaction, with the kink limiting the ring's ability to thread and dethread from one side of the axle. Under steady-state irradiation, the photo-isomerization drives transitions of the axle between Z and E isomers (Fig. 1), thereby biasing the kinetics of the ring's diffusion along the axle. The authors use ^{1}H NMR to measure concentrations of the chemical species in the non-equilibrium steady state generated under in situ irradiation with a constant photon flux at four different intensities. Those concentrations reflect that the molecular 'pump' preferentially pushes the ring along the axle in one direction. That operation has been studied in the past; what is particularly novel about this work is that the authors combine the measurements with new theoretical calculations and interpretations.

Previous theoretical efforts have analysed how supramolecular machines use a thermodynamic driving force to break detailed balance. One line of inquiry has proposed rate models to interrogate the microscopic origin of the kinetic asymmetry that determines the direction of motion[4]. A parallel body of theoretical work grew into the field of stochastic thermodynamics[5], a framework that clarifies how concepts such as heat, work and entropy production behave in small fluctuating systems. That stochastic thermodynamic perspective offered a natural route to incorporate the role of information in nanoscale machines, yielding new understanding of the thermodynamics of information[6]. Drawing from the stochastic thermodynamic lessons, information thermodynamics has also been applied to chemical reaction networks with deterministic rather than stochastic kinetics[7,8]. Viewed through that lens of information thermodynamics, the rotaxane motor[1] can be thought of as two different subsystems statistically coupled together: one consisting of light-driven photo-isomerization steps and the other consisting of thermal motion of the ring.

The authors suggest that an efficiency for the artificial machine is related to the free-energy exchanges between the two subsystems — how strongly do the photo-excited transitions force the coupled ring-translation coordinates? As illustrated in Fig. 1, the photo-excited degrees of freedom resemble a heat engine in that they are simultaneously in contact with a solvent bath and with light behaving like a hot bath. The new work is striking in that it quantifies, directly from experimental measurements, the efficiency of transferring the free energy from the isomerization step into the pumping.

Having done all the hard work of fitting rate models and interpreting the information thermodynamics, one might hope to arrive at an unambiguous answer as to whether or not the pump is efficient and good. Unfortunately, the situation is not so simple. Unlike a protein pump embedded in a membrane, this pump is incapable of performing work. The rings are pulled from a well-mixed solution onto the axle from one side, then are pushed back into the same solution from the other side of the axle. Indeed, in a sense it is that futility of the pump that demands that the efficacy be thought of in some manner other than a traditional thermodynamic efficiency. The photons directly affect the E/Z distribution, pushing the relative concentration of the isomers away from its equilibrium. That disequilibrium in turn biases the likelihood that an axle is threaded by a ring, forcing a flux in what would

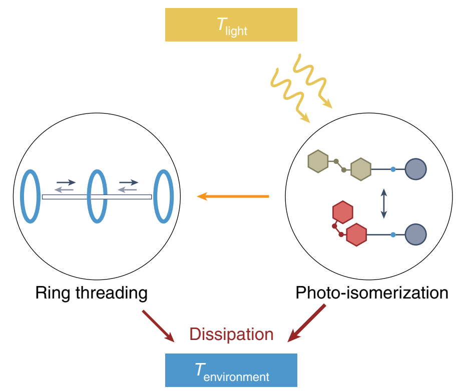

Fig. 1 | Light-driven rotaxane 'machine'. An irradiated rotaxane acts like an artificial machine in contact with solution at a temperature $T_{environment}$ and a much higher effective temperature associated with the light, T_{light}. Although this driving force directly biases the photo-isomerization, coupling between the isomer shape (upper isomer, E form; lower isomer, Z form) and ring threading results in net flux of a macrocyclic ring across the axle of the rotaxane. Under steady-state irradiation, both isomerization and ring-threading motion dissipate heat into the environment at the same rate light adds energy into the system, and the relative size of the two dissipations is suggested as a measure for how efficiently the supramolecular pump transduces free energy between the two types of motion (orange arrow).

otherwise be a thermal equilibrium between threaded and unthreaded configurations. The authors quantitatively show that higher light intensity pushes the proportion of threaded and unthreaded axles further from equilibrium. In that irradiated steady state, the non-equilibrium system accepts energy from the photons and dissipates that energy as heat into the solution. Some fraction of that heat dissipation arises directly from the isomerization events and some fraction arises indirectly from the ring motion.

The efficiency, constructed as the ratio of those two processes' dissipations, thus serves as a figure of merit for the coupling between photo-isomerization and pumped rings. That the figure of merit can be extracted from steady-state experiments is a considerable advance in connecting experiments with theory, but it also identifies important questions for the future. Can the pumps be synthesized in such a manner that they can be made to do work, akin to a cross-membrane protein pump? How might the information thermodynamic analysis of a zero-work futile pump inform the performance of the pump under a load? And how general can the lessons be when the kinetics cannot be decomposed into a bipartite graph[9]? ❐

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Competing interests

The author declares no competing interests.