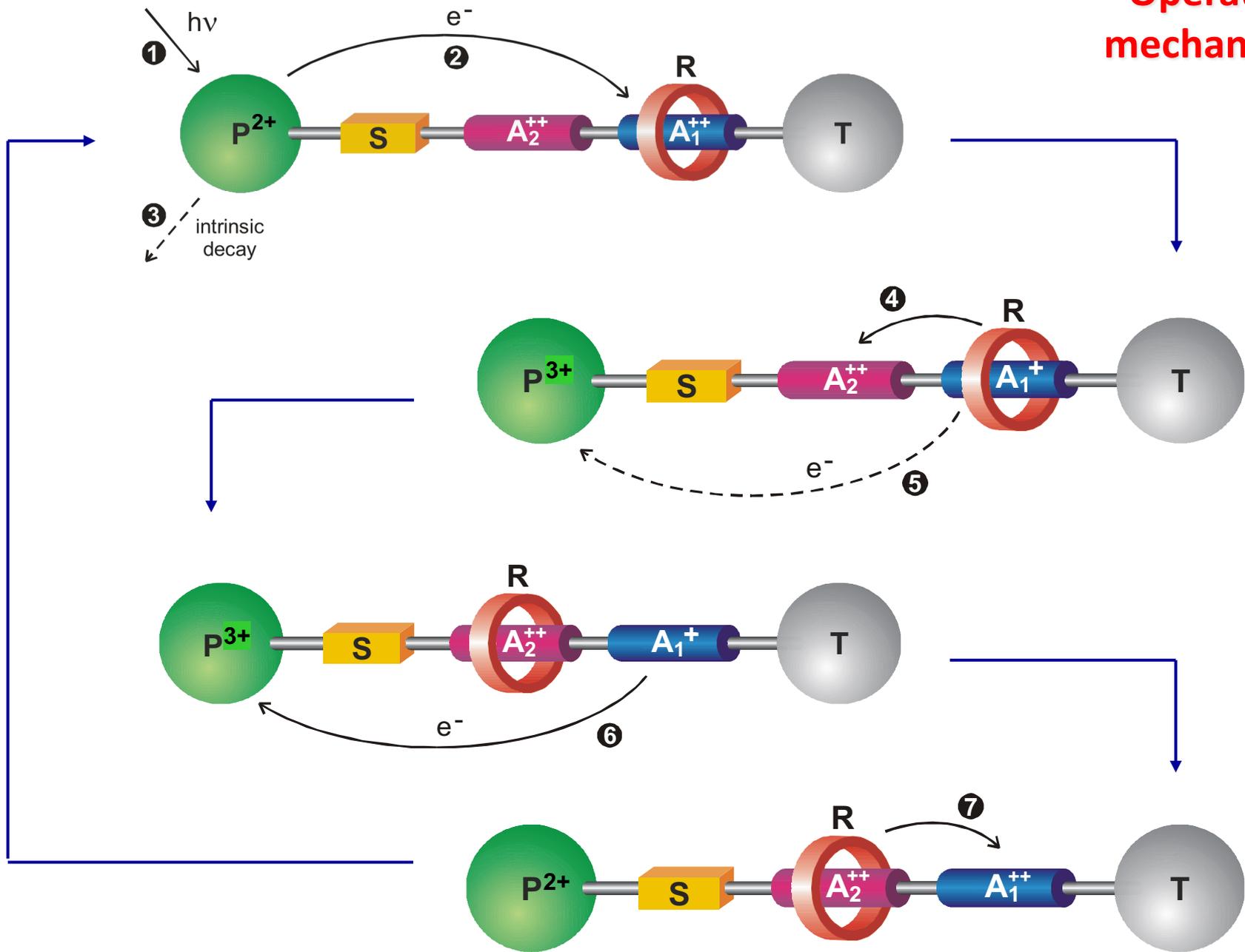
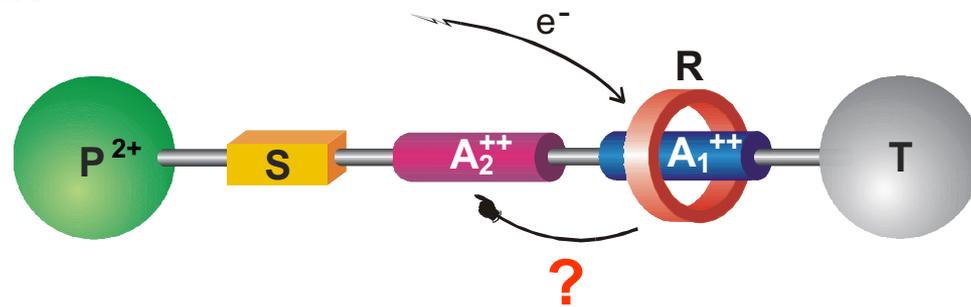


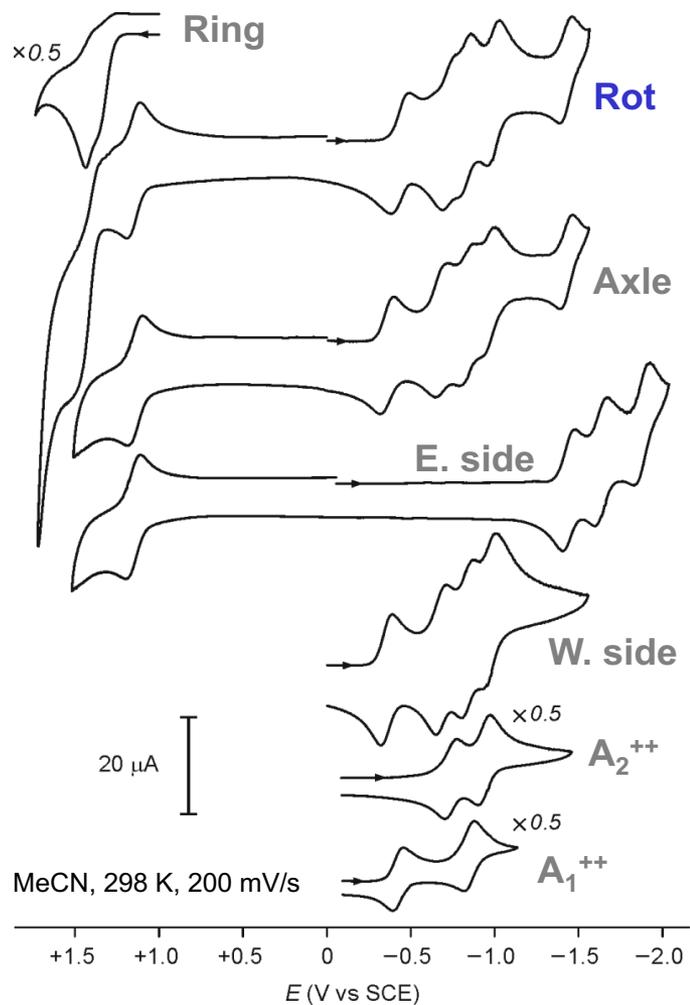
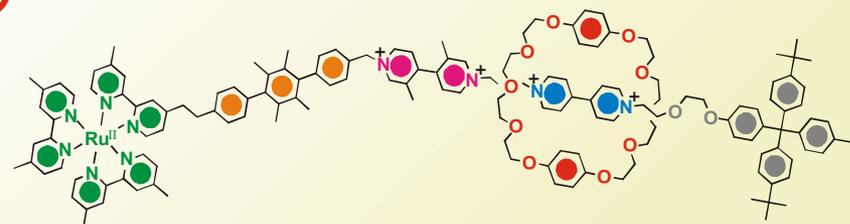
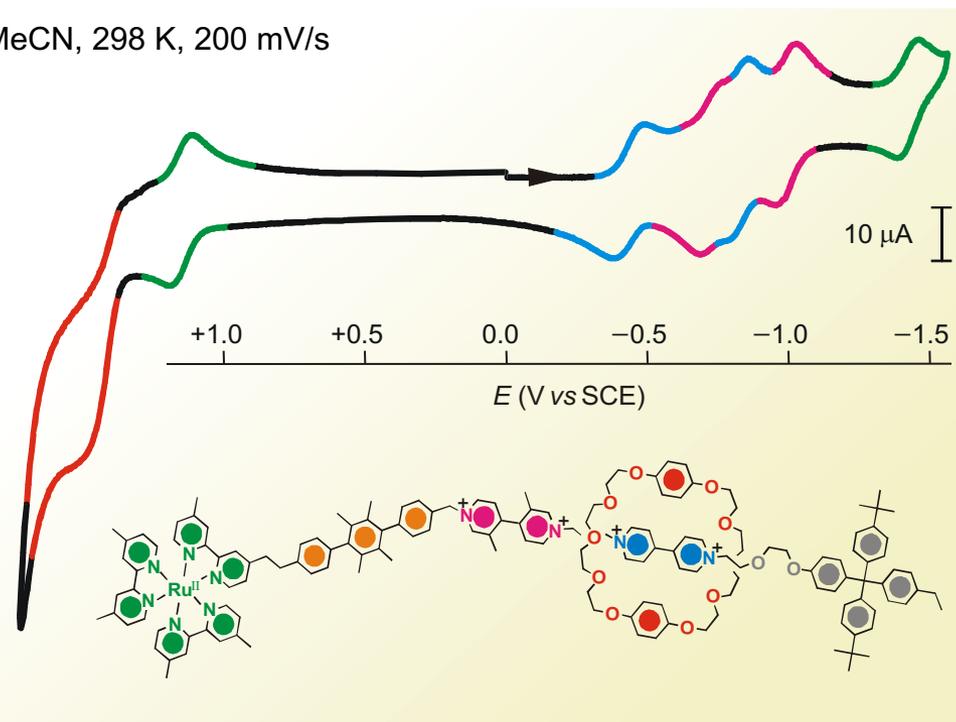
Operation mechanism



Redox-induced ring displacement



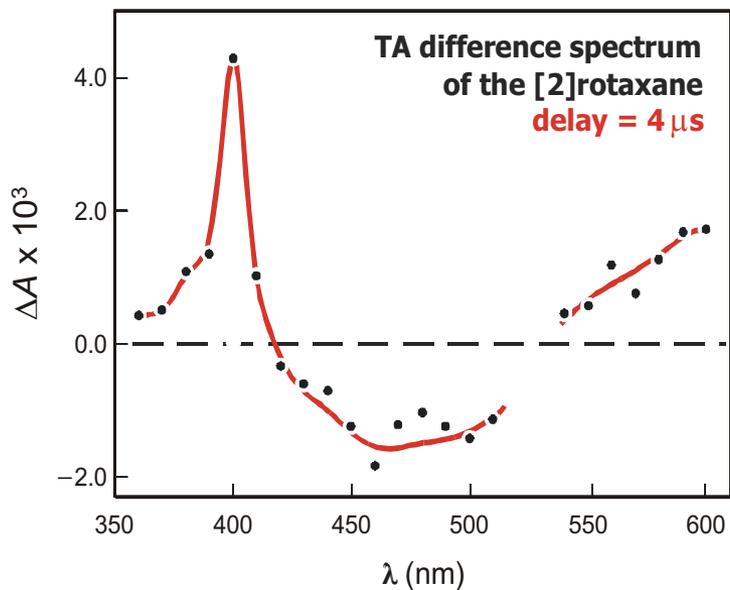
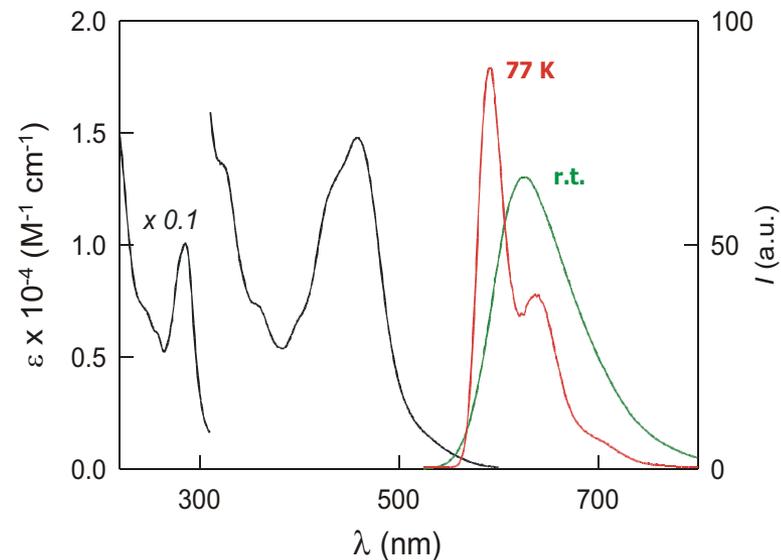
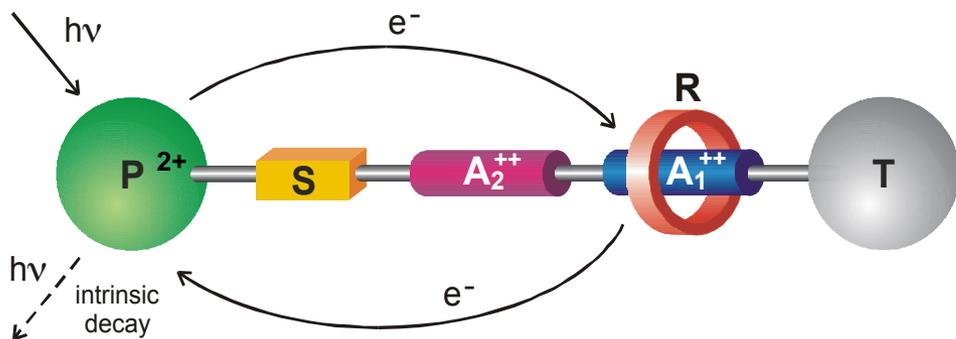
MeCN, 298 K, 200 mV/s



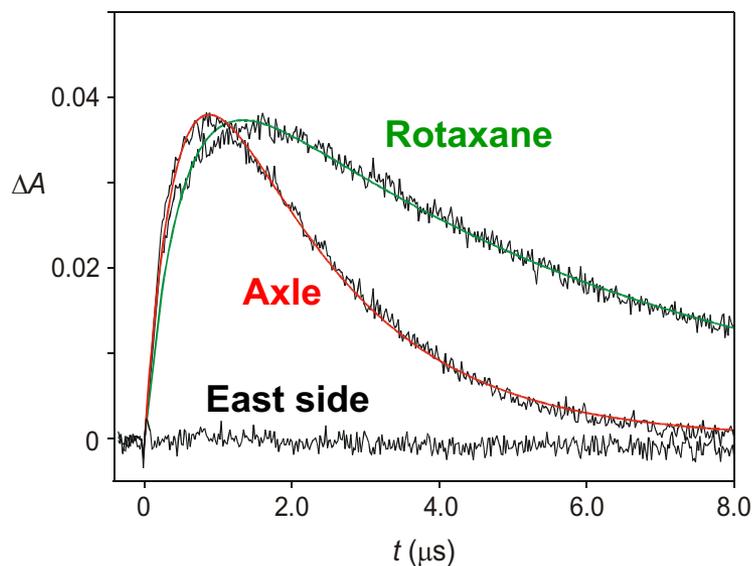
Eléna Ishow
Miguel Clemente-Leon

Chem. Eur. J. **2000**, *6*, 3558
Acc. Chem. Res. **2001**, *34*, 445
J. Phys. Chem. B **2003**, *107*, 14319
Pure Appl. Chem. **2005**, *77*, 1051

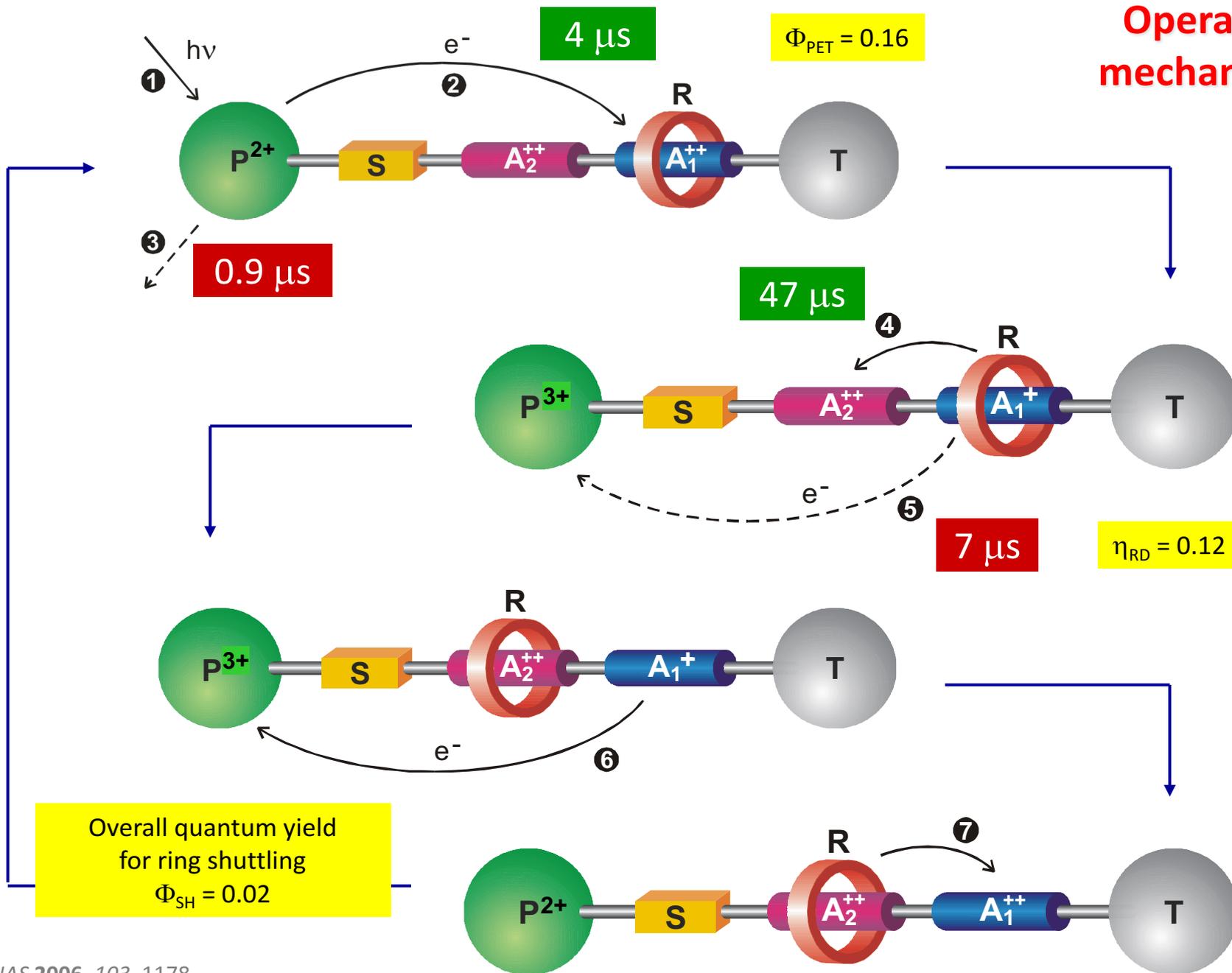
Photoinduced electron transfer



MeCN, RT
exc@532 nm



Operation mechanism



Autonomous artificial nanomotor powered by sunlight

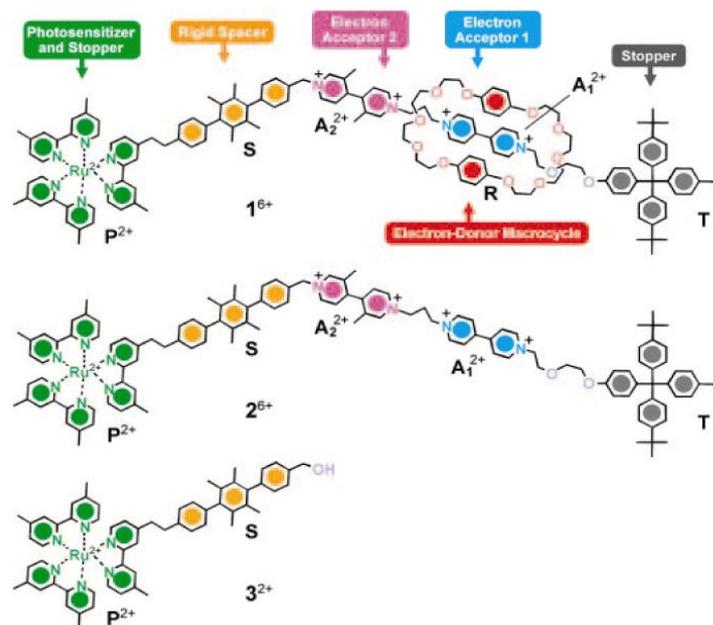
Vincenzo Balzani^{†‡}, Miguel Clemente-León^{†§}, Alberto Credi^{†‡}, Belén Ferrer^{†¶}, Margherita Venturi[†], Amar H. Flood^{||}, and J. Fraser Stoddart^{†||}

[†]Dipartimento di Chimica "G. Ciamician," Università di Bologna, via Selmi 2, 40126 Bologna, Italy; and ^{||}California NanoSystems Institute and Department of Chemistry and Biochemistry, 405 Hilgard Avenue, University of California, Los Angeles, CA 90095

Edited by Jack Halpern, University of Chicago, Chicago, IL, and approved December 6, 2005 (received for review October 14, 2005)

Light excitation powers the reversible shuttling movement of the ring component of a rotaxane between two stations located at a 1.3-nm distance on its dumbbell-shaped component. The photoinduced shuttling movement, which occurs in solution, is based on a "four-stroke" synchronized sequence of electronic and nuclear processes. At room temperature the deactivation time of the high-energy charge-transfer state obtained by light excitation is $\approx 10 \mu\text{s}$, and the time period required for the ring-displacement process is on the order of 100 μs . The rotaxane behaves as an autonomous linear motor and operates with a quantum efficiency up to $\approx 12\%$. The investigated system is a unique example of an artificial linear nanomotor because it gathers together the following features: (i) it is powered by visible light (e.g., sunlight); (ii) it exhibits autonomous behavior, like motor proteins; (iii) it does not generate waste products; (iv) its operation can rely only on intramolecular processes, allowing in principle operation at the single-molecule level; (v) it can be driven at a frequency of 1 kHz; (vi) it works in mild environmental conditions (i.e., fluid solution at ambient temperature); and (vii) it is stable for at least 10^3 cycles.

molecular machine | nanoscience | photochemistry | rotaxane | supramolecular chemistry



Scheme 1. Structural formulas of rotaxane 1^{6+} , its dumbbell-shaped component 2^{6+} , and model compound 3^{2+} .

NATURE | Vol 440 | 16 March 2006

PHOTOCHEMISTRY

Lighting up nanomachines

Euan R. Kay and David A. Leigh

A cleverly engineered molecule uses light to generate a charge-separated state and so cause one of its components to move. It's the latest study of a molecular machine that exploits nature's most plentiful energy source.

Nature runs the nanomachinery that makes life possible using the last word in clean, free and readily available power sources — sunlight. In photosynthetic bacteria and green plants, photon absorption by chlorophyll generates a charge-separated state, from which the electron is quickly passed down a cascade of electron carriers, ultimately generating energy in a convenient chemical form. Can similar capabilities be engineered? An exemplary effort to do just this is given by Balzani *et al.* who, writing in *Proceedings of the National Academy of Sciences*, describe photochemical experiments on an artificial machine that uses light to displace a fragment of its unimolecular structure.

Those who seek to harness the Sun's energy for synthetic molecular machines find that chemistry is always throwing up obstacles. In particular, charge recombination typically occurs thousands or millions of times faster than the nuclear movements on which such machines rely, making charge-separated states difficult to exploit. This problem can be overcome using bimolecular systems: here, the charged partners quickly diffuse apart so their energy can be used, for example, to achieve

switching in a rotaxane¹. This class of molecule, consisting of a ring that shuttles randomly and incessantly along a string, stopped only by bulky groups at the string's termini, is also that used by Balzani and colleagues².

Their rotaxane¹ (Fig. 1) incorporates two structurally different bipyridinium sites — 'stations' 1 and 2 — that slow the shuttling ring's motion through strong short-range electrostatic interactions. The ring thus divides its time between station 1, station 2 and the rest of the string in the ratio of around 95:5:1. At room temperature, the ring shuttles between the stations tens of thousands of times per second, but the net flux is zero. So no work can be done, or useful task performed, by the shuttling action (the 'principle of detailed balance'³).

One of the bulky end-groups of the rotaxane's string is a ruthenium tris(bipyridine) complex. This can absorb a photon of visible light and so form a reactive, excited state that donates an electron to the more easily reduced of the two bipyridinium sites — station 1, the ring's preferred binding site. One would normally expect the resulting charge imbalance to be corrected by back-transfer of an electron on

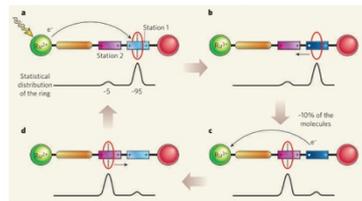


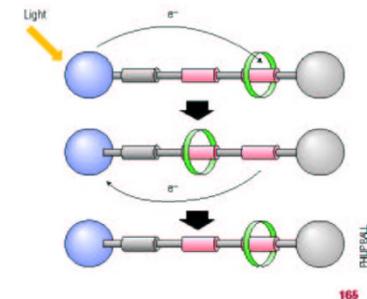
Figure 1 Light-driven molecular shuttle. Balzani and colleagues' rotaxane¹ consists of a molecular ring free to move along a molecular string. **a**, At equilibrium in the ground state, the ring spends most of the time over station 1, as a result of attractive, non-covalent interactions. But irradiation of the ruthenium complex (green) at one end of the string generates a highly reducing excited state, resulting in electron transfer to station 1, and the weakening of this station's electrostatic interactions with the ring. **b**, Normally, charge recombination is fast in comparison with nuclear motions, but here a delay allows approximately 10% of the molecules to undergo significant Brownian motions, shifting the distribution of these rings to favour station 2. **c**, When charge recombination eventually does take place, the higher binding affinity of station 1 is restored, and **d**, the system reduces to restore the original statistical distribution of rings.

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Making light work of it

In contrast to motors in nature, artificial ones generally require one input to cause motion, followed by another to reset the motor. Often these inputs are chemical fuels, and therefore generate waste products, as well as requiring intervention at each stage. Now Balzani *et al.* report an autonomous motor powered simply with light (*Proc. Natl. Acad. Sci.* **103**, 1178–1183; 2006). The motor consists of a rotaxane — a ring threaded around a dumbbell-shaped component of two electron-acceptor sites, or 'stations', for the ring to move between, with a bulky stopper group on each end. Absorption of a photon at

a stopper group initiates electron transfer to the station where the ring rests, causing displacement to the second station. An electron can then transfer back to the stopper group from the now-free first station, and the ring can return to its original position. The motor works analogously to a four-stroke engine, with fuel injection and combustion, piston displacement, exhaust removal and piston-replacement steps. The motors of Balzani *et al.* rely exclusively on intramolecular processes and light absorption, and therefore do not consume chemical fuel or produce waste.



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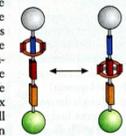
IP

SCIENCE & TECHNOLOGY

CONCENTRATES

Light drives molecular motor

A molecular motor powered by sunlight alone has been prepared by chemists in Italy and in the U.S. (*Proc. Natl. Acad. Sci. USA* **2006**, *103*, 1178). Vincenzo Balzani and Alberto Credi of the University of Bologna, J. Fraser Stoddart of the University of California, Los Angeles, and their coworkers believe their device is unique for several reasons. Because it's powered solely by visible light, the motor's movement—the shuttling of a crown ether back and forth between two points on the handle of a dumbbell-shaped structure (shown)—requires no additional chemicals and produces no waste products. Also, the shuttle's movement relies on intramolecular processes, so it could, in principle, be operated at the single-molecule level. The motor moves when a ruthenium complex (green sphere) at one end of the dumbbell absorbs a photon and transfers an electron to a 4,4'-bipyridinium moiety (blue bar) within the dumbbell's handle. This reduction prompts the crown ether (pink circle) to move 1.3 nm to a 3,3'-dimethyl-4,4'-bipyridinium unit (red bar) in the compound. The crown ether moves back to its original position via a back electron-transfer process.



subjected the protein to an approach called SIAFE (simultaneous incorporation and adjustment of functional elements) in conjunction with directed evolution (iterative modification and selection for desirable activity). The result was evMBL6, a designed enzyme with the ability to hydrolyze β -lactam amide bonds, a type of activity on which bacterial resistance to β -lactam antibiotics is based. Key to the change was the replacement of several of the enzyme's surface loop structures. The researchers say they hope the technique can be extended to convert other structures into enzymes that catalyze diverse reactions, including some not found in nature.

Down-to-earth NMR spectrometry

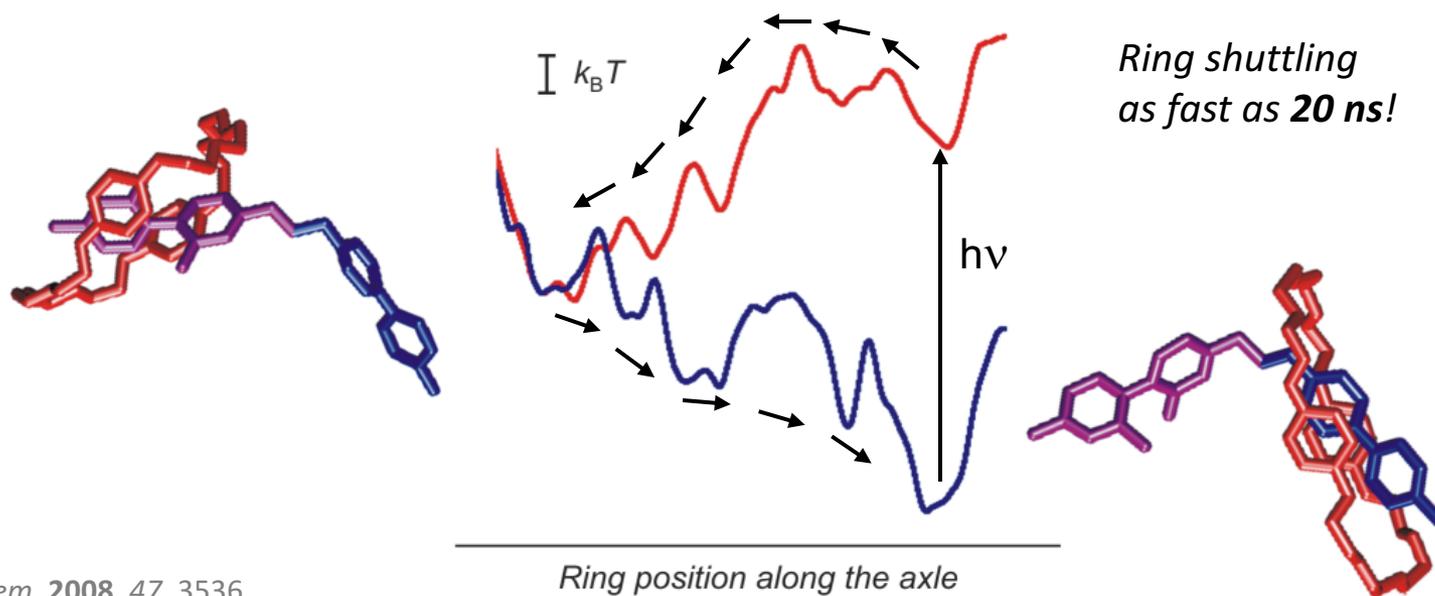
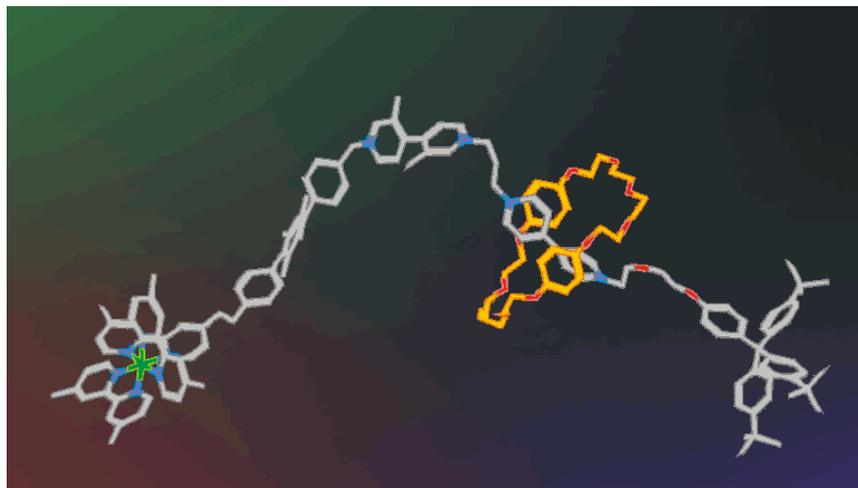
Small

Synthetic procedures

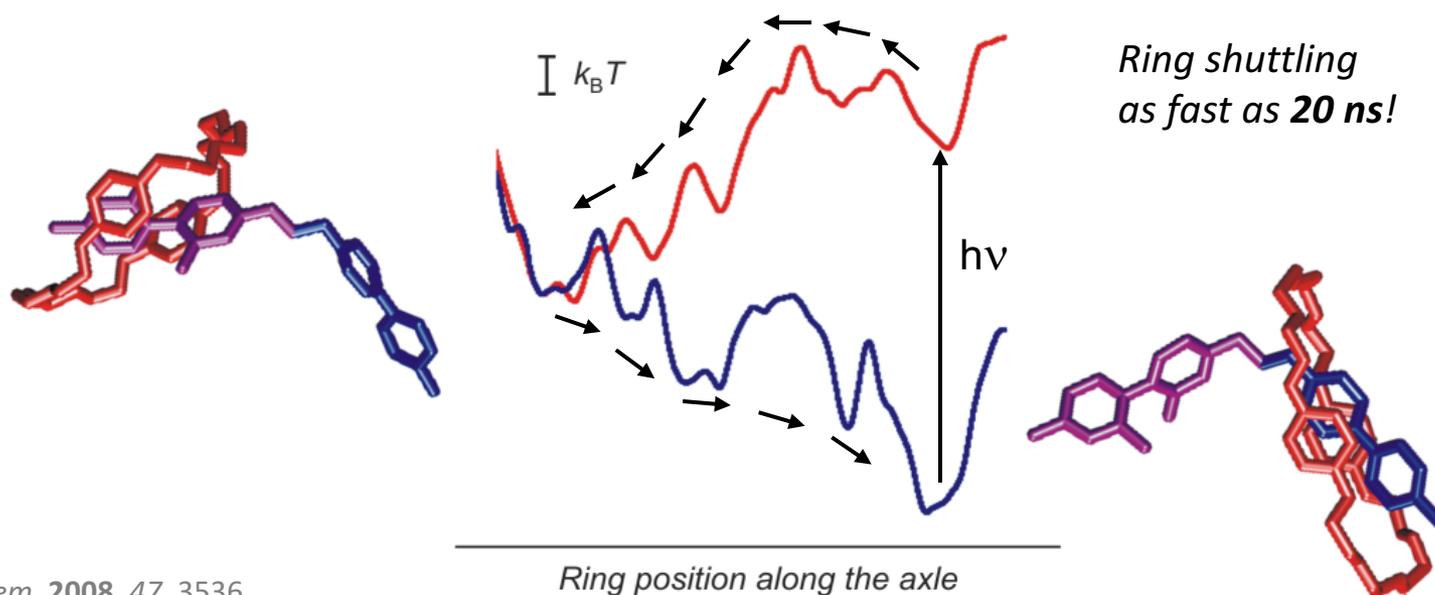
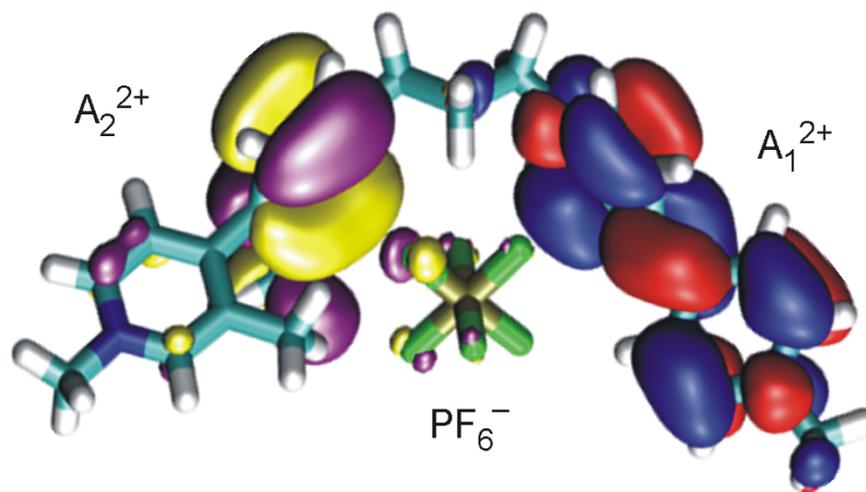
Nano Motor Powered by Solar Energy

Chemists at the University of Bologna (Italy), UCLA, and the California NanoSystems Institute (both USA) have designed and constructed a rotaxane-based molecular motor of nanometer size that is powered only by sunlight. The system is built up from a dumbbell-shaped component, which is more than 6 nm long, and a ring component of a diameter of approximately 1.3 nm. The ring component is trapped on the rod portion by two bulky stoppers, which are attached to the ends of the rod so that the ring cannot slip off. The rod portion of the dumbbell contains two "stations" that can be called "A" and "B". The absorption of sunlight by one of the two stoppers, a light-harvesting species, causes the transfer of one electron to station A, which is deactivated as far as wanting

Collaboration with
Paolo Raiteri and
Michele Parrinello,
ETH Zürich

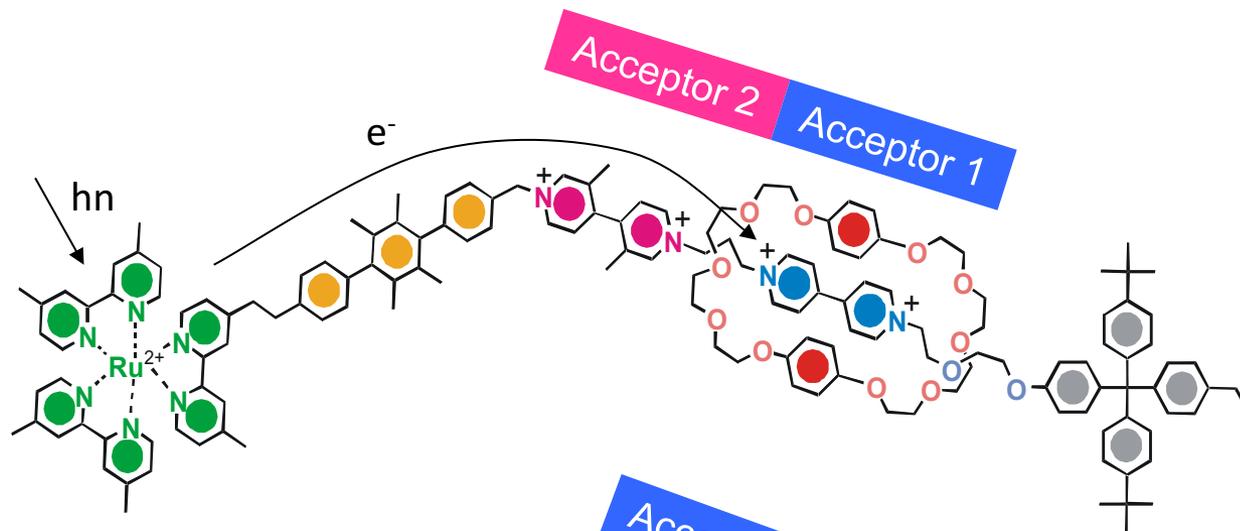


Collaboration with
Paolo Raiteri and
Michele Parrinello,
ETH Zürich

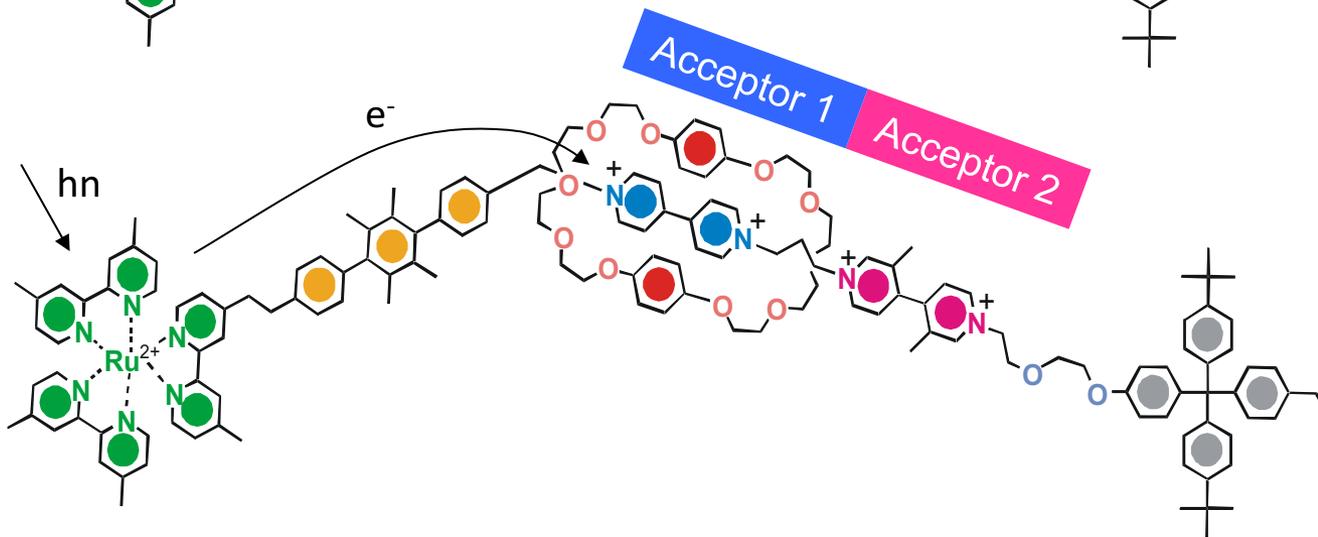


Exchanging the position of the stations

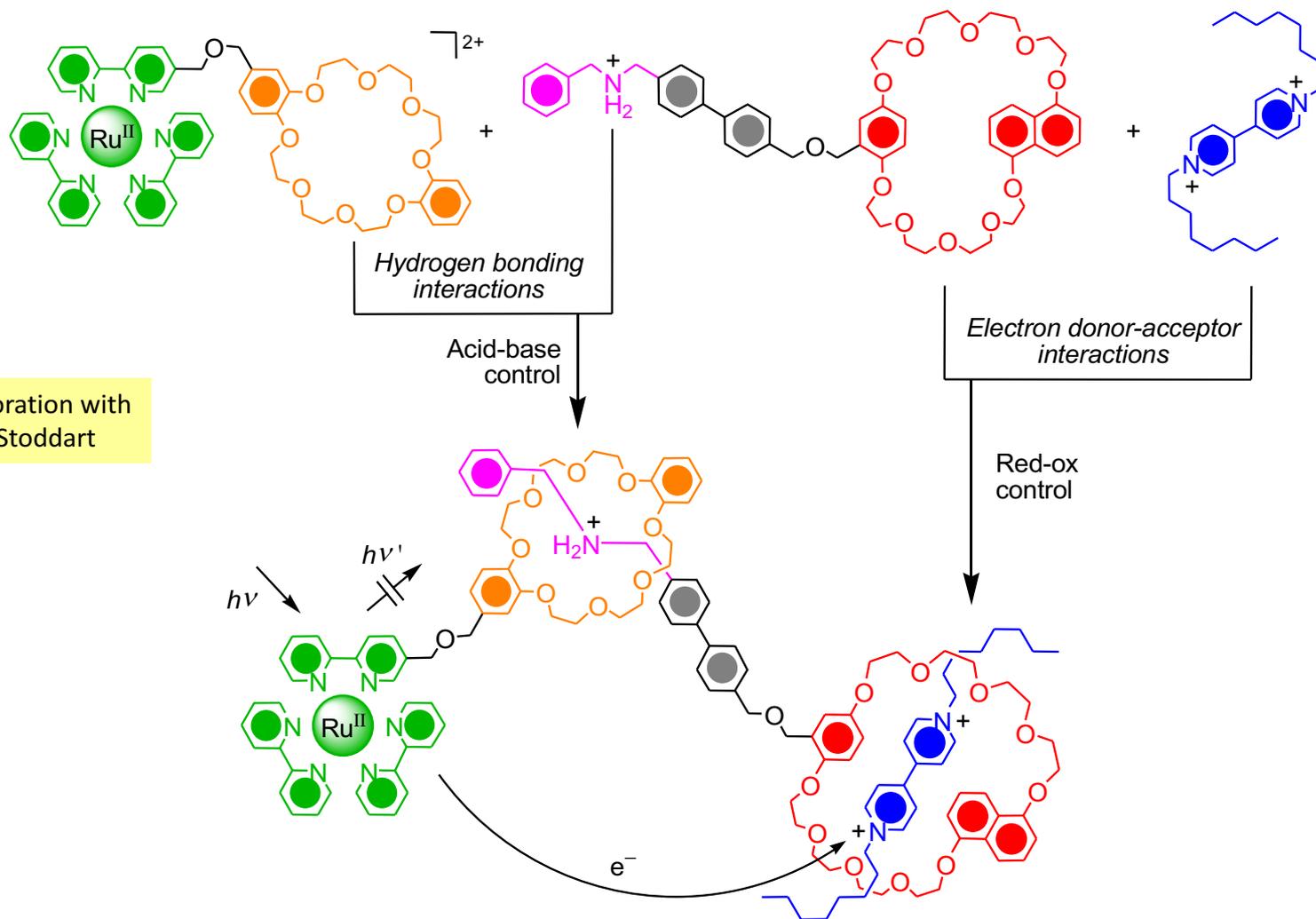
$\Phi_{\text{PET}} = 0.16$



$\Phi_{\text{PET}} = 0.50$

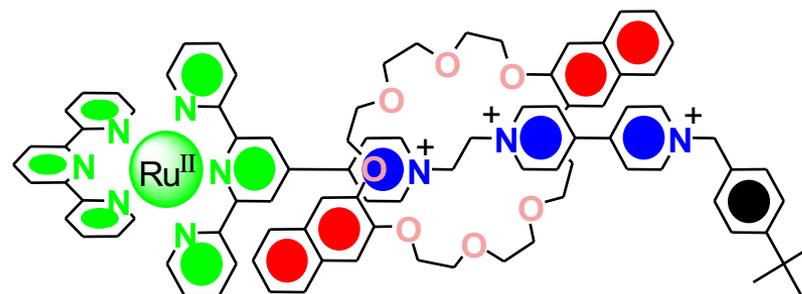
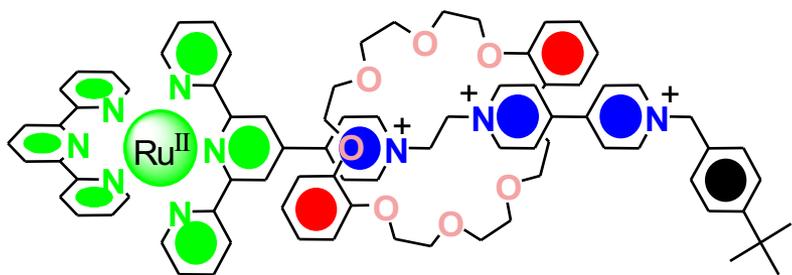
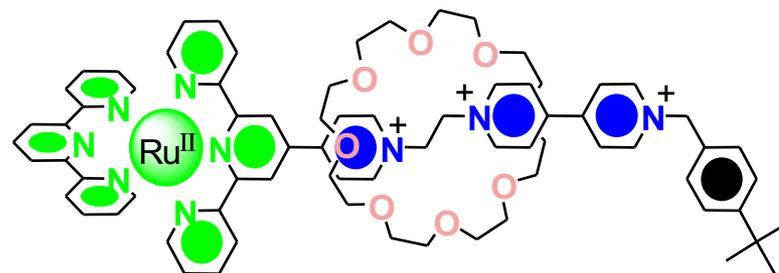
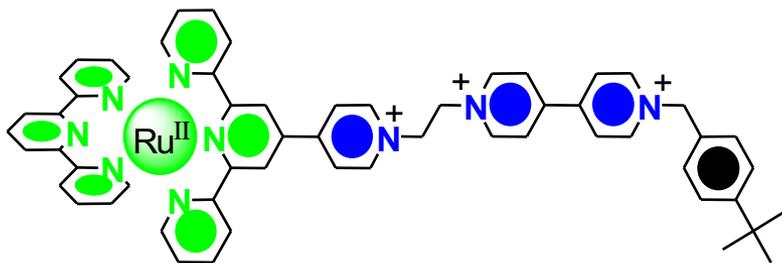


Connecting the photosensitizer in a noncovalent manner



Collaboration with
Fraser Stoddart

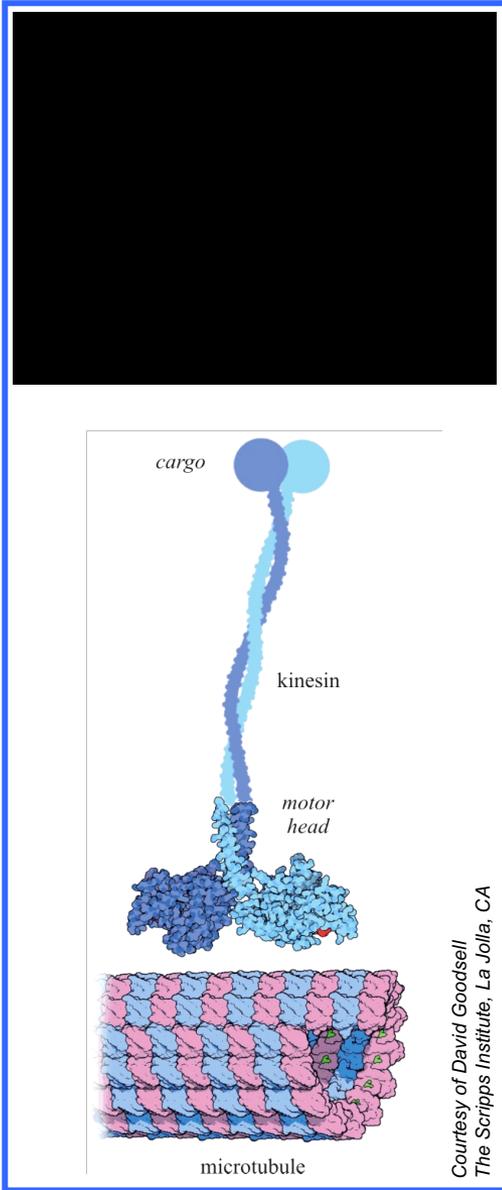
Exploiting different metal complex photosensitizers



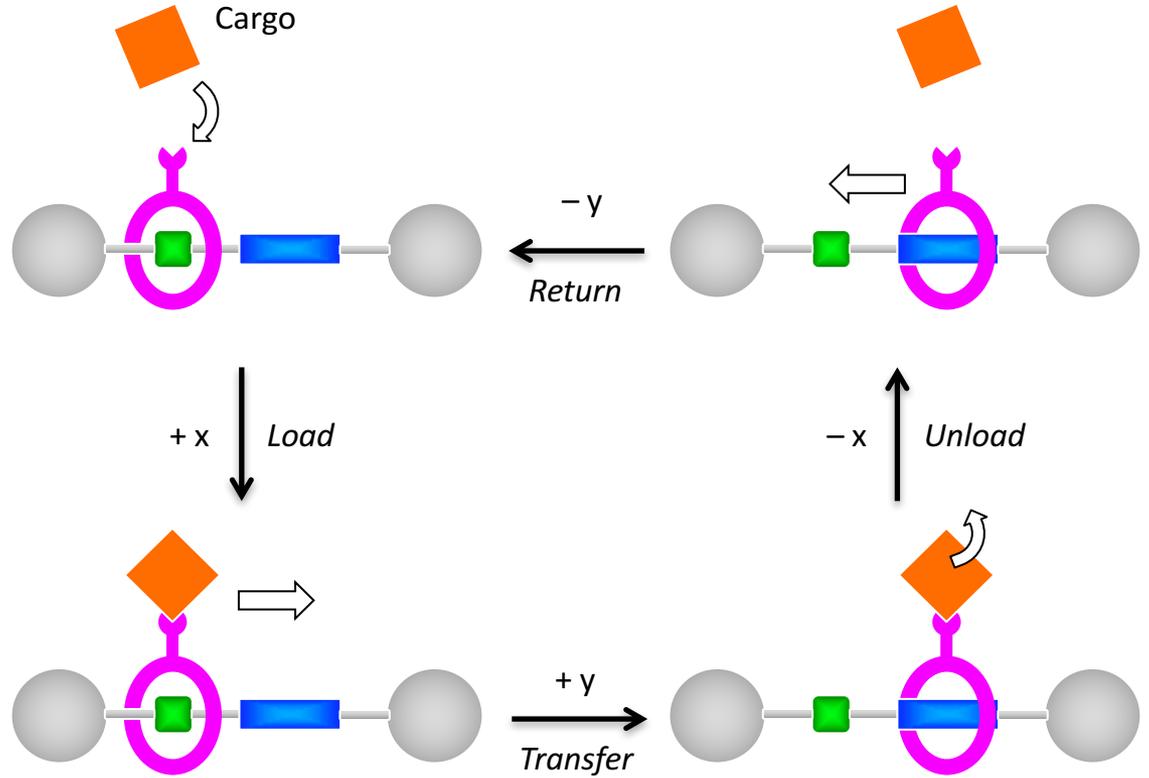
Collaboration with Steve Loeb
University of Windsor, Canada

Paolo Passaniti, Serena Silvi

Chem. Eur. J. **2006**, *12*, 3233



Towards artificial molecular transporters



Kinesin motor-based transport

Towards artificial molecular transporters

Inorg. Chem. **2004**, *43*, 8346-8354

Photochemical Expulsion of the Neutral Monodentate Ligand L in $\text{Ru}(\text{Terpy}^*)(\text{Diimine})(\text{L})^{2+}$: A Dramatic Effect of the Steric Properties of the Spectator Diimine Ligand

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