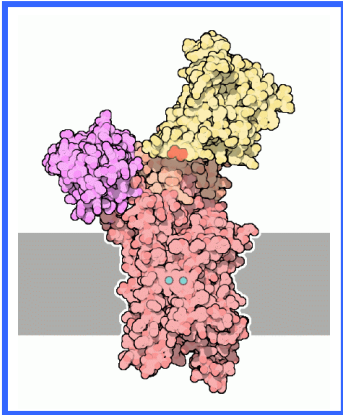
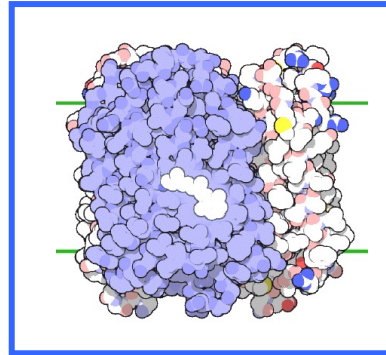


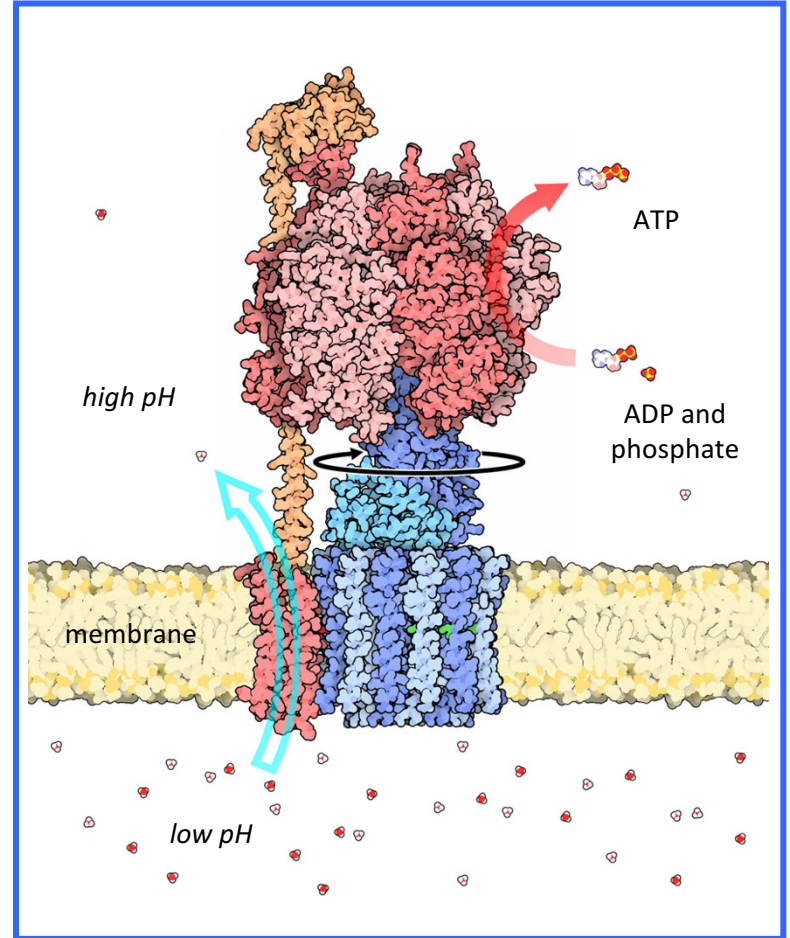
Naturally occurring molecular machines



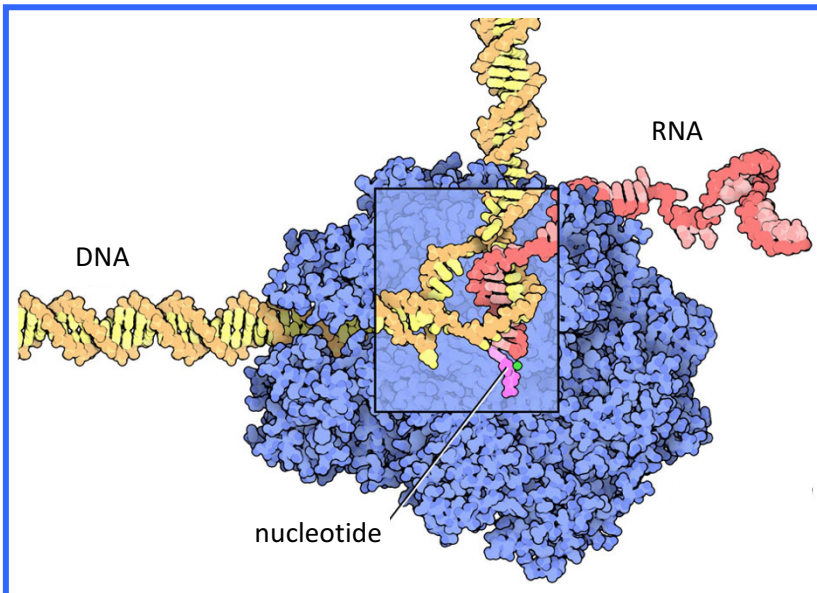
Calcium pump



Bacteriorhodopsin



ATP Synthase



RNA Polymerase

Synthetic molecular motors

Anthony P. Davis

The construction of miniature, 'nanoscale' machines is a goal of modern science and technology, inspired by Richard Feynman's remark that "There's plenty of room at the bottom"¹. Chemists, by the nature of their discipline, are already at the bottom, manipulating the smallest entities that have complex shapes (molecules), and which can therefore be used as engineering components. While engineers and physicists explore the top-down approach to nanoscale engineering through lithography and scanning probe microscopy, chemists are well placed to pursue the bottom-up strategy, whereby molecular-scale components are created using chemical synthesis and then self-assembled into devices by pre-programmed intermolecular forces².

Among the more interesting challenges in this area is the design and synthesis of 'molecular actuators', molecules that can undergo changes in shape in response to external stimuli and thereby, in principle, perform mechanical work. To date, most research has concentrated on two-state systems, ranging from classical *cis-trans* isomerism to more elaborate 'rotaxanes' and 'catenanes' (Fig. 1)^{3,4}, and biomolecular constructs, such as a device based on the transition of right-handed to left-handed DNA⁵. These systems, in which movement is driven by chemical, electrochemical or photochemical forces, are best described as molecular

switches or shuttles, and they have great potential in, for example, molecular-scale information processing. However they are not capable of the continuous, unidirection-

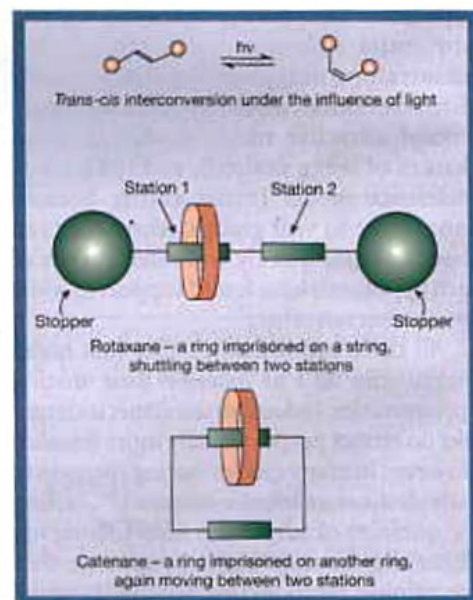
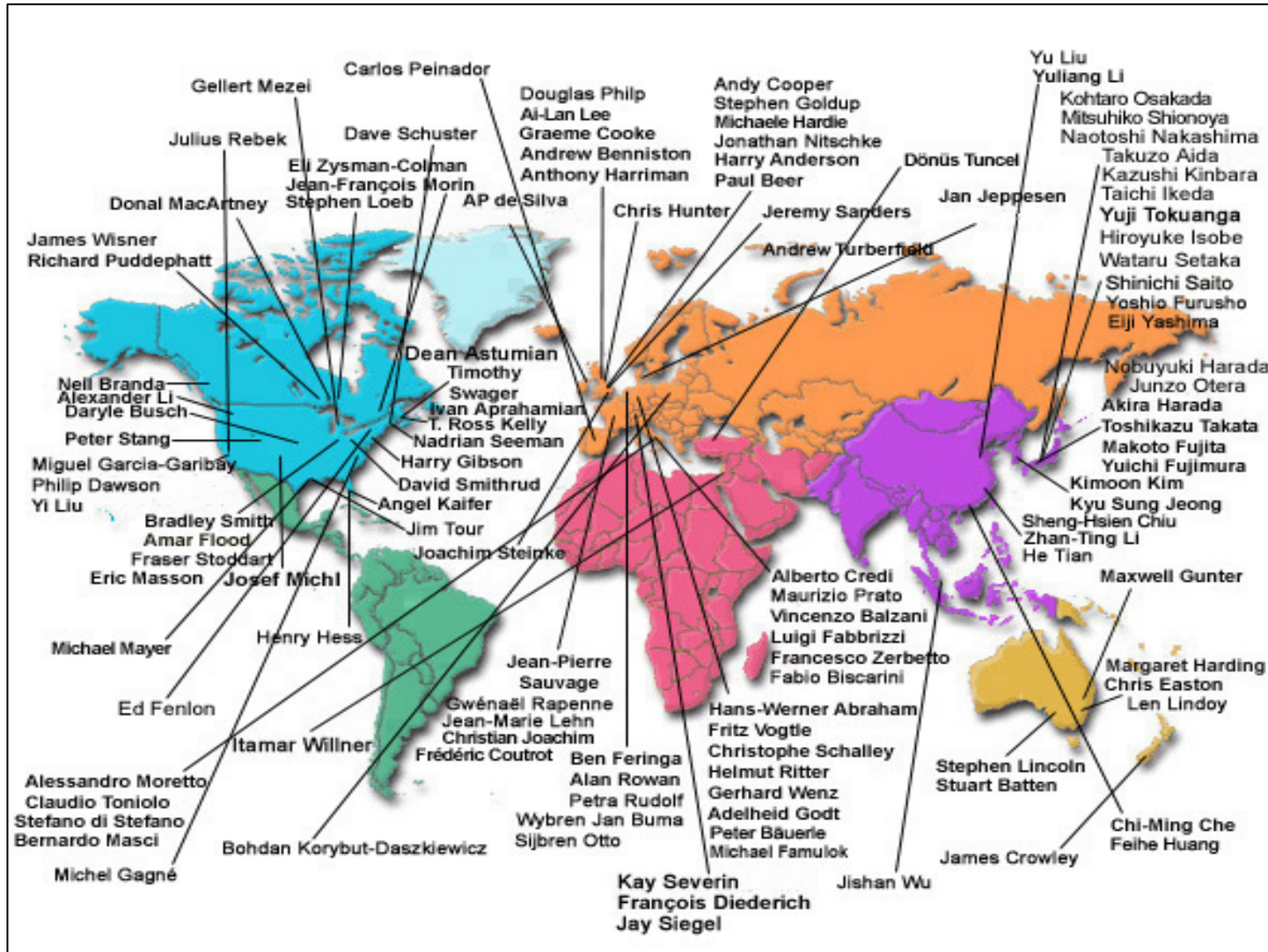
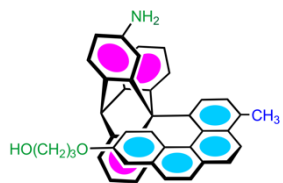


Figure 1 **Two-state molecular systems.** Established molecular actuators include systems capable of *cis-trans* isomerism, where groups lie on the same (*cis*) or opposite (*trans*) sides of a double bond, and more complex structures such as rotaxanes and catenanes. The rings in the rotaxanes and catenanes may be driven between stations by chemical, electrochemical or photochemical input.

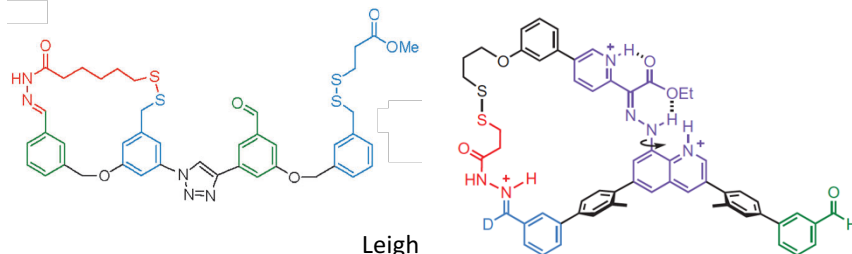
The geography of research on molecular machines



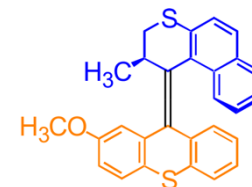
Artificial molecular machines



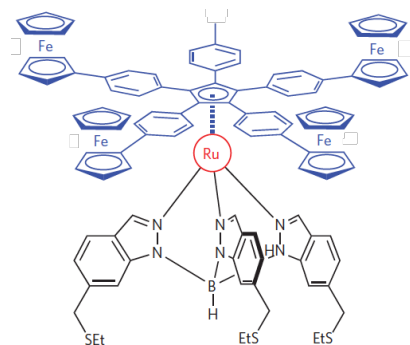
Kelly



Leigh

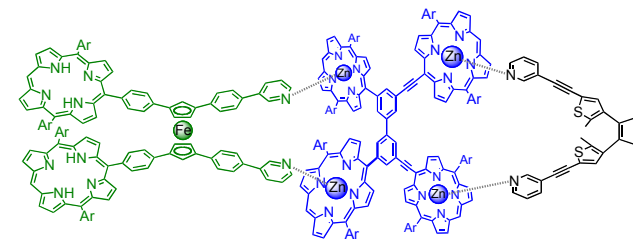
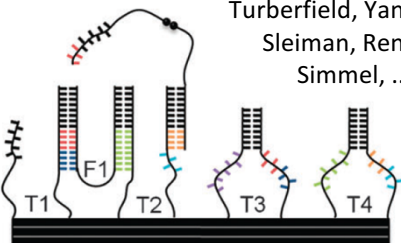


Feringa

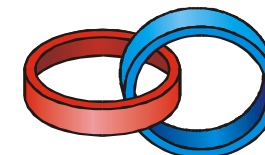
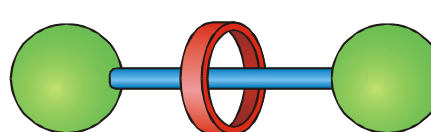


Joachim, Rapenne

Seeman, Mao, Willner, Famulok,
Turberfield, Yan,
Sleiman, Ren,
Simmel, ...



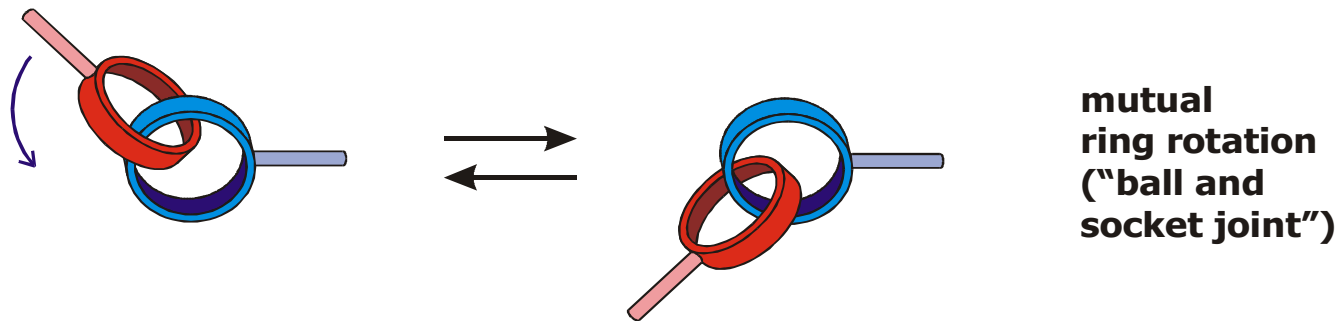
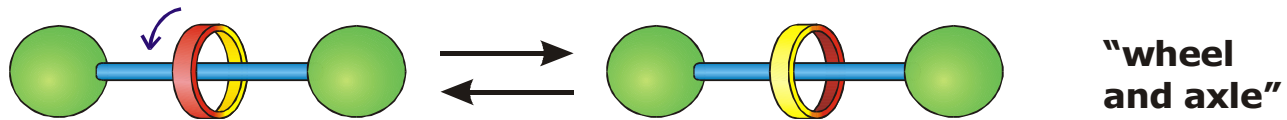
Aida



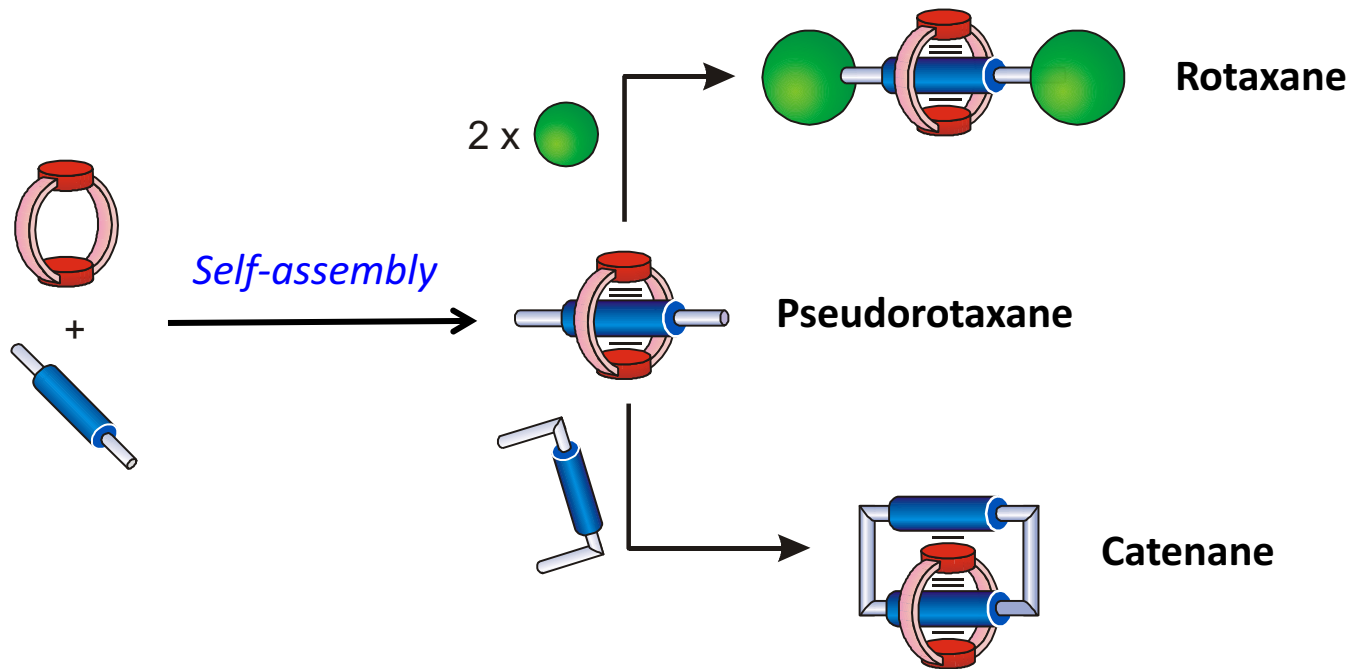
Other systems: Lehn, Huc, Yashima, Haberhauer,
Hecht, Tamaoki, Shionoya, Michl, Giuseppone,
Herges, Garcia-Garibay, Aprahamian, ...

Sauvage, Stoddart, Leigh, Kim, Harada, Tian, Kaifer, Willner, Nolte, Loeb,
Beer, Huang, Paolucci, Brouwer, Tuncel, Coutrot, Flood, Hirose, ...

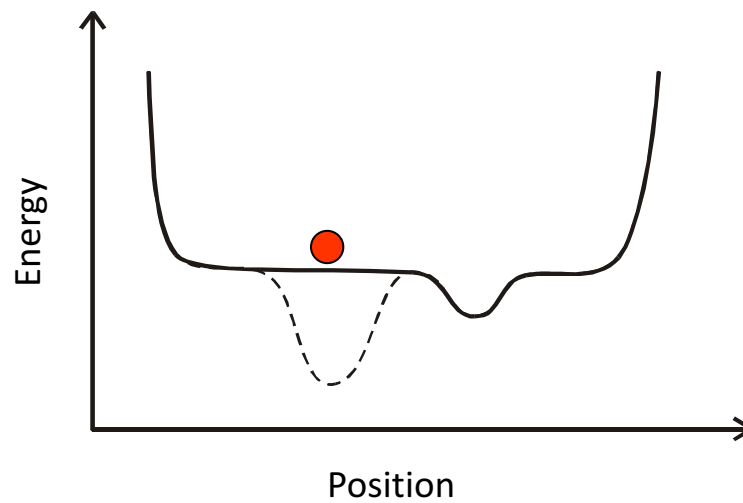
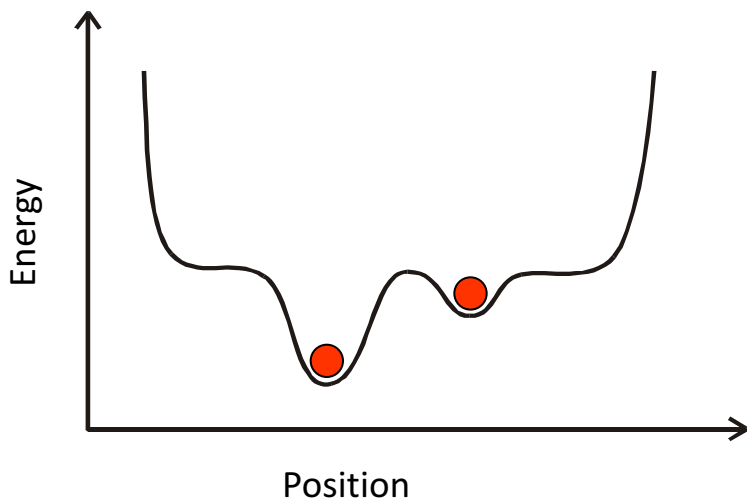
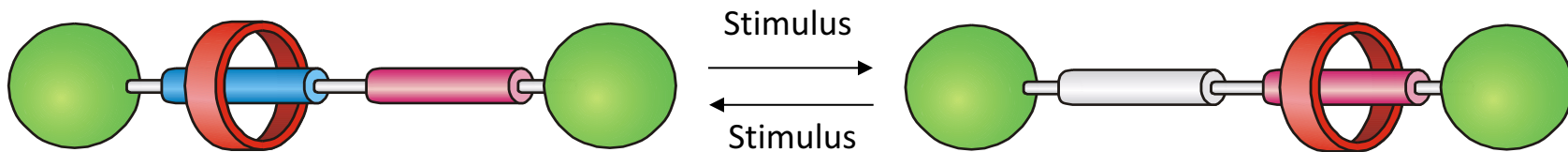
Rotaxanes and catenanes as molecular machines



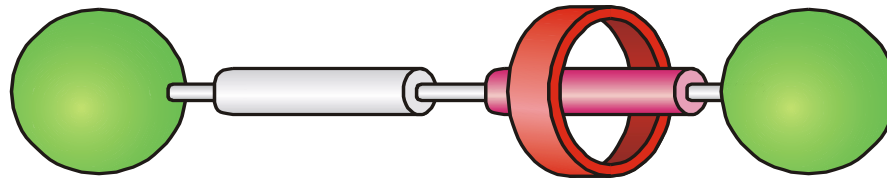
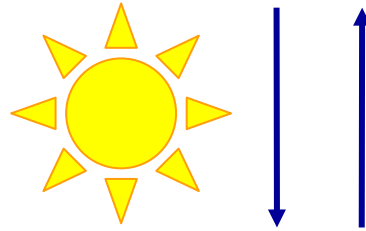
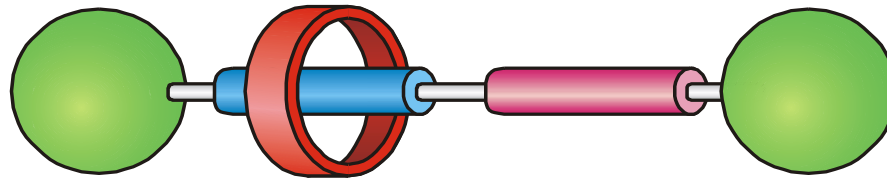
Synthesis of rotaxanes and catenanes



Linear motions in rotaxanes: design of a molecular shuttle

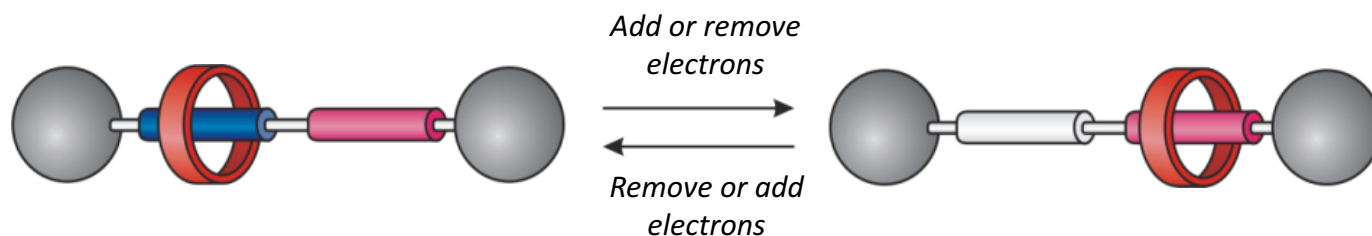


A nanomachine powered by sunlight

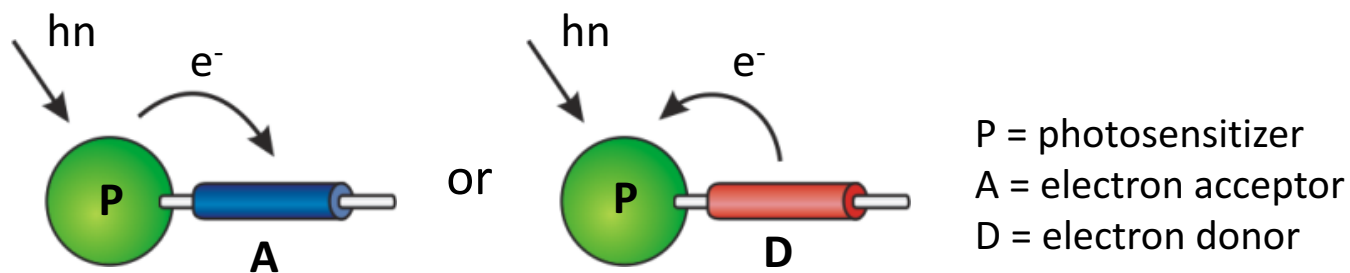


A molecular shuttle based on photoinduced electron transfer

a) Redox-driven molecular shuttle



b) Multicomponent system for photoinduced electron transfer



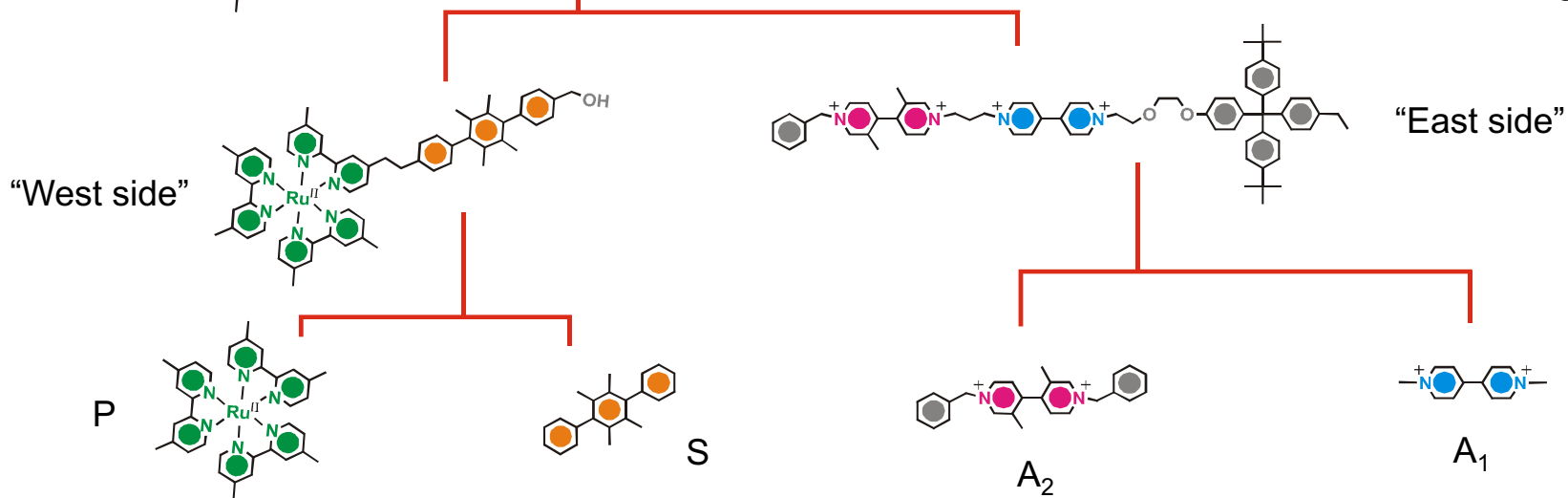
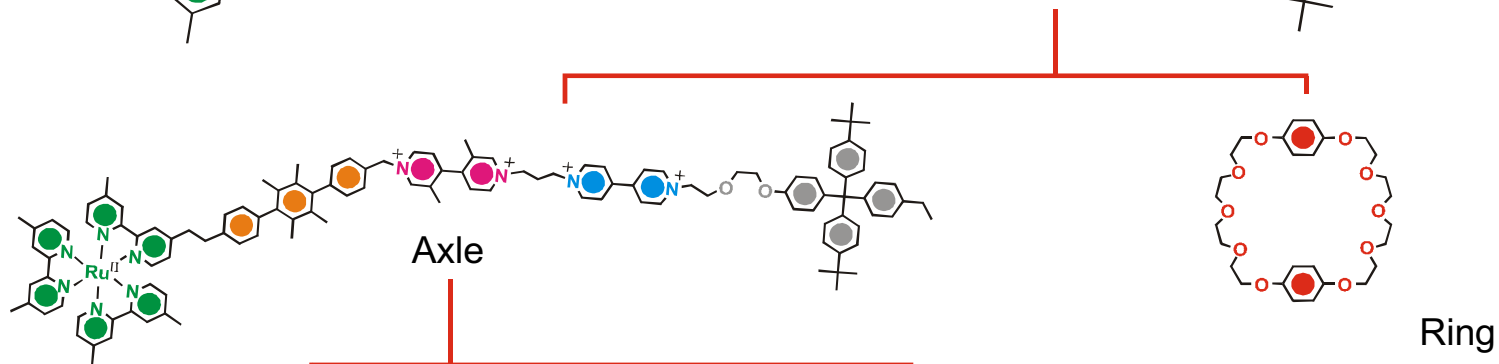
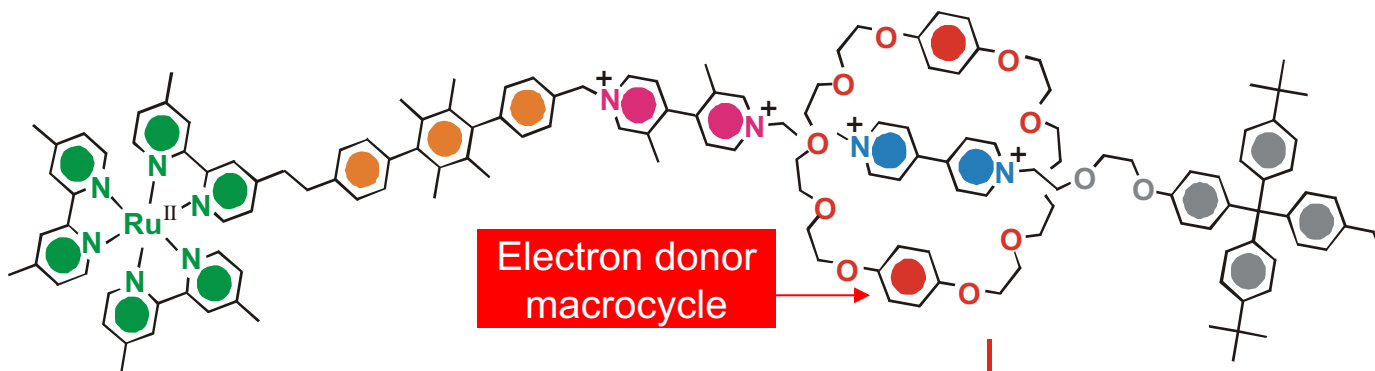
Photosensitizer
and stopper

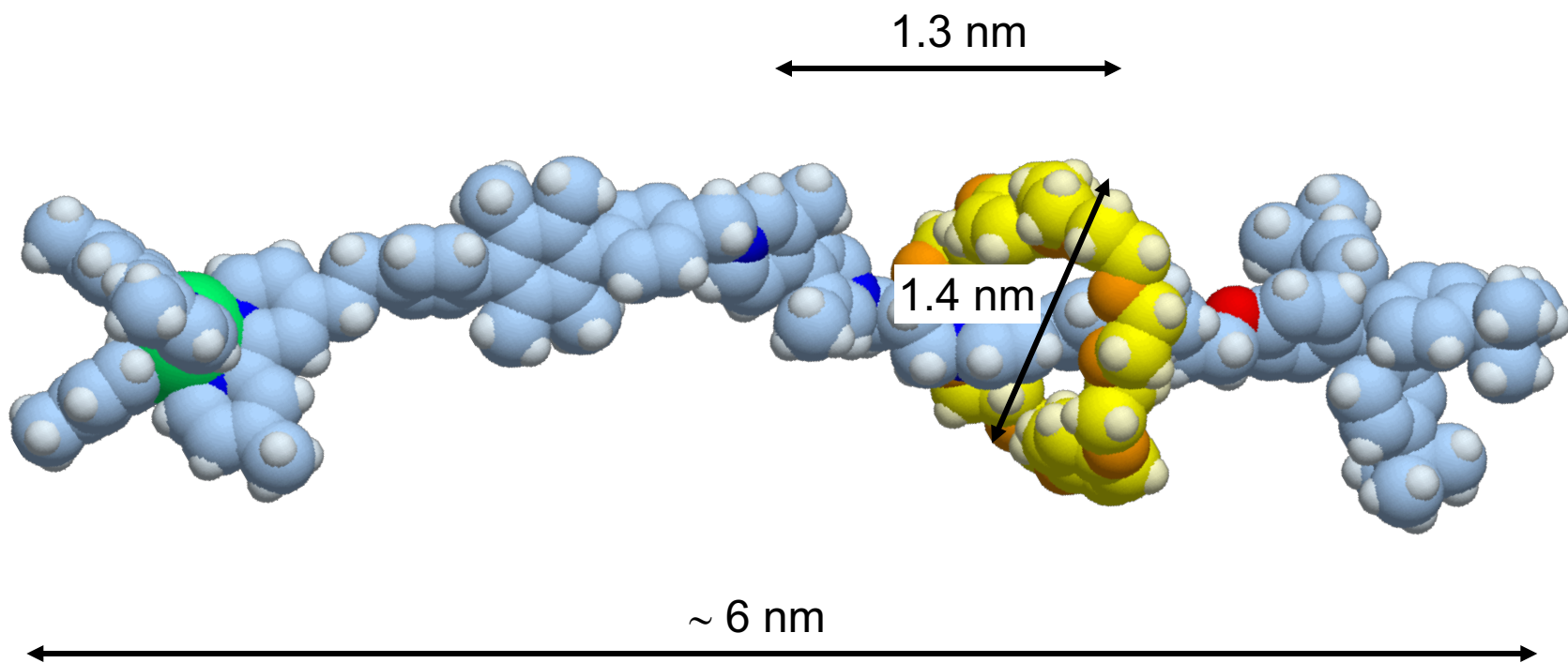
Rigid
spacer

Electron
acceptor 2

Electron
acceptor 1

Dumb
stopper





The outstanding photophysical and redox properties of $\text{Ru}(\text{bpy})_3^{2+}$

