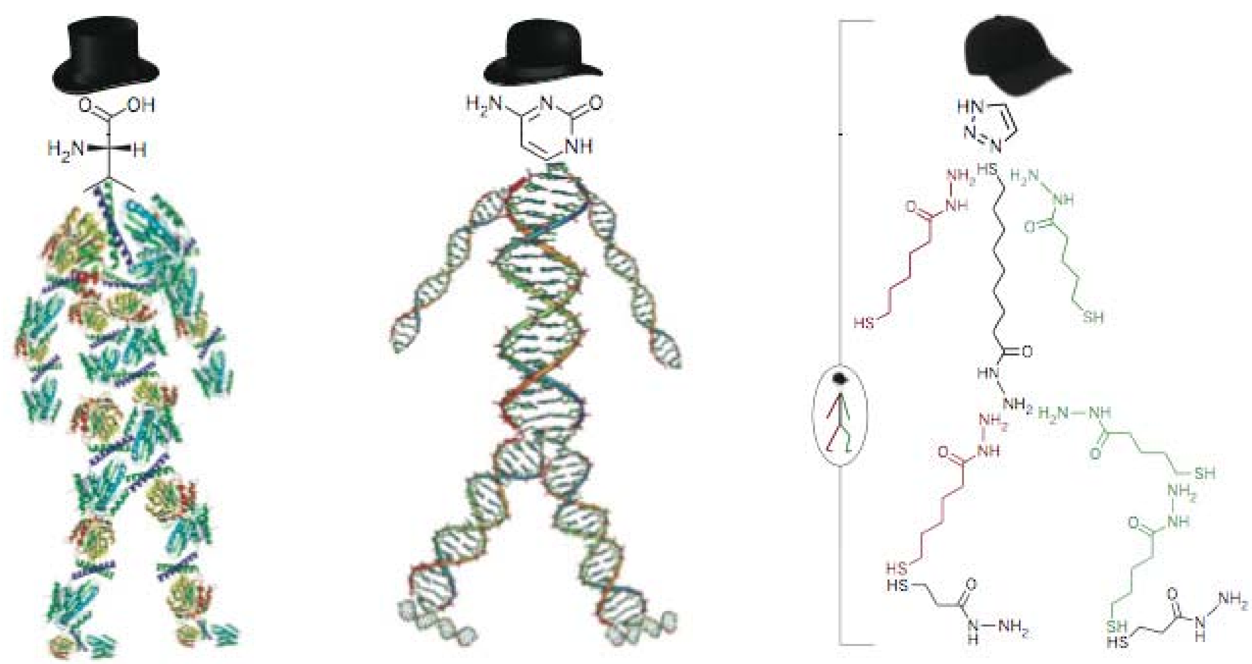
Walking Molecules



Biological protein walkers　　Artificial DNA walkers　　Artificial small-molecule walkers

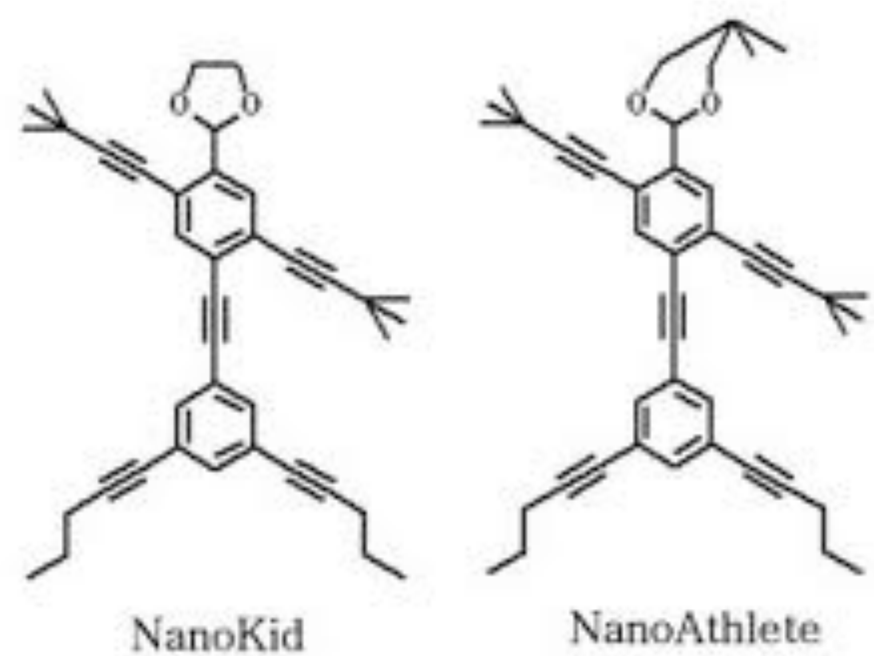
Lit. Seminar
11.5.31(Tue.)
Katsuya SATO(M1)

Table of Contents

prof. D. Leigh

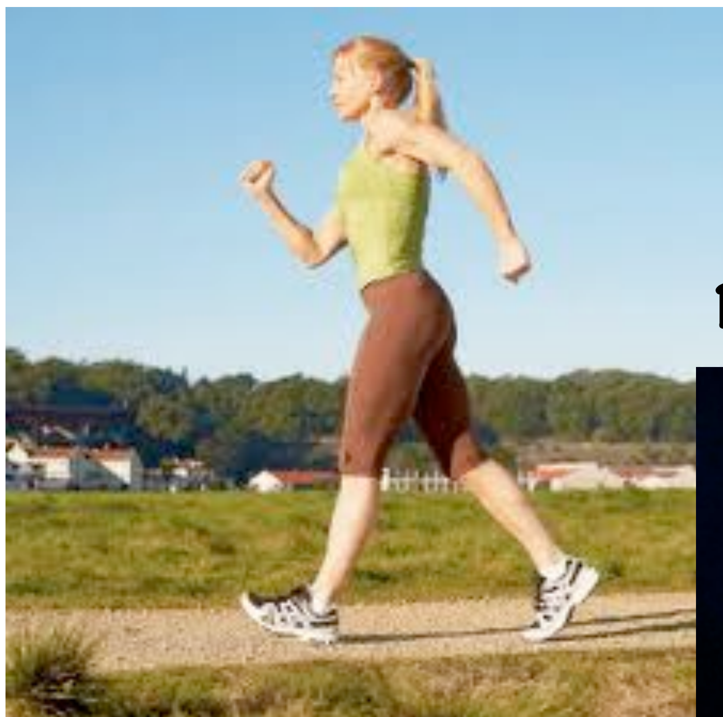
see review : D. Leigh *Chem. Soc. Rev.* **2011**, ASAP (DOI:10.1039/c1cs15005g)

I. Introduction



Introduction

- What is “walking” ?



She walks along the “road” to “forward”.

But he walks back.

Why they walk on the “ground” not on the “wall” or “ceiling”?

Introduction

- Walking needs...

  a. Processivity : the ability to remain attached to the track

  b. Directionality : migration preferentially or exclusively towards one end of the track

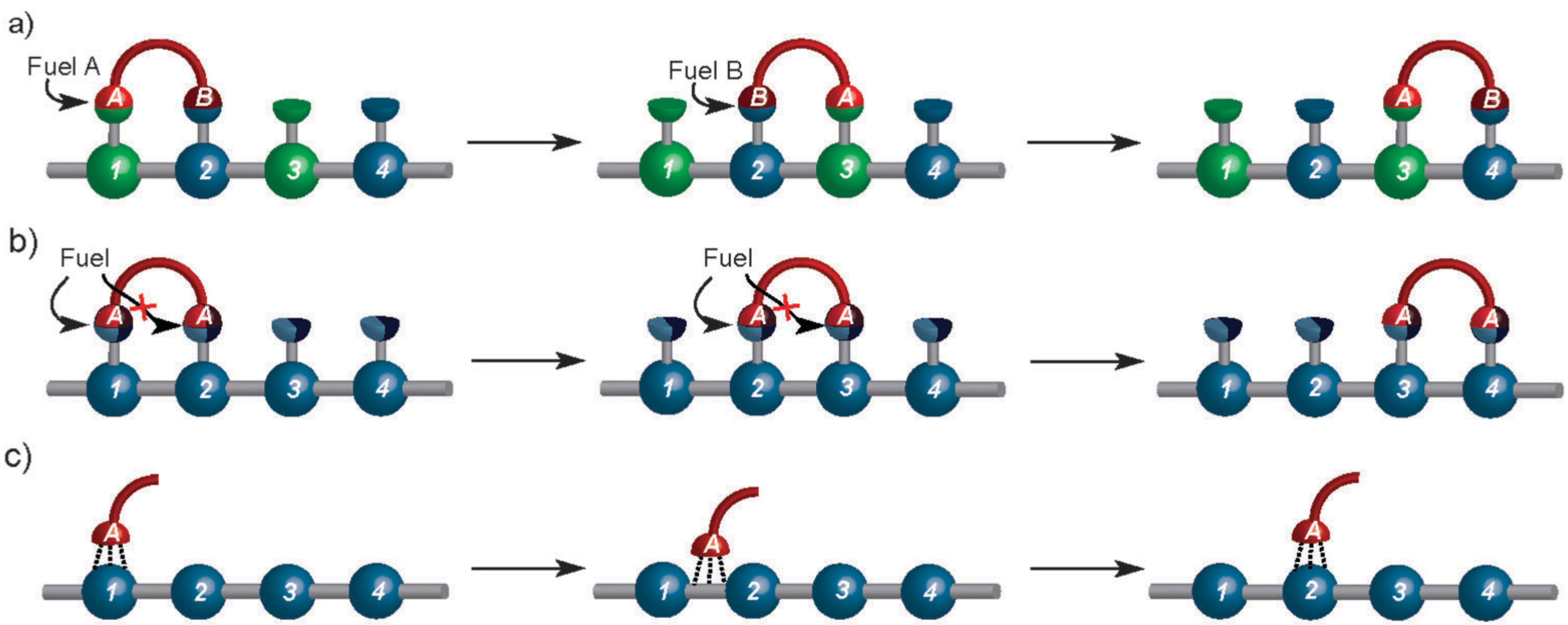
  c. Repetitive operation : the ability to repeatedly perform similar mechanical cycles

  d. Progressive operation : the capability to be reset at the end of each mechanical cycle without undoing the physical task that was originally performed

  e. Autonomous operations : the ability to continually function as long as an energy input is present

Processivity

- To achieve processivity



a) two different feet, two different fuels/conditions
b) two identical feet, the fuel with asymmetric interaction
c) one-legged walker with secondary interactions

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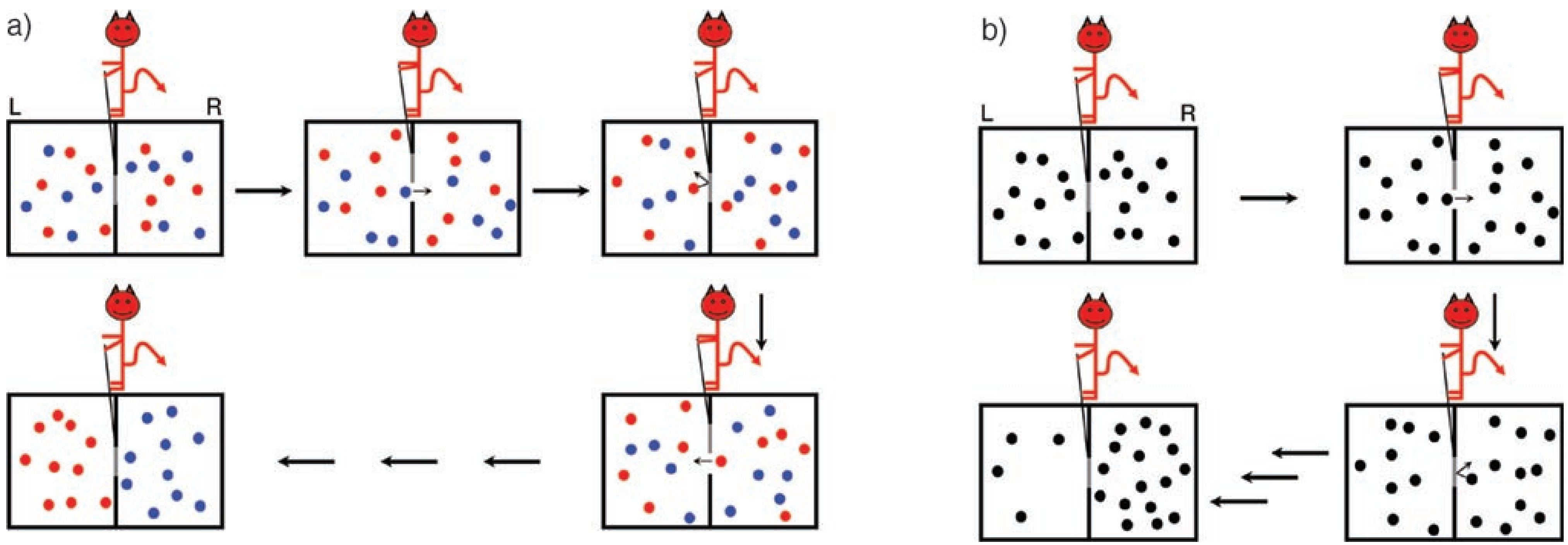
Directionality

- Maxwell's "Demon"



a) temperature demon

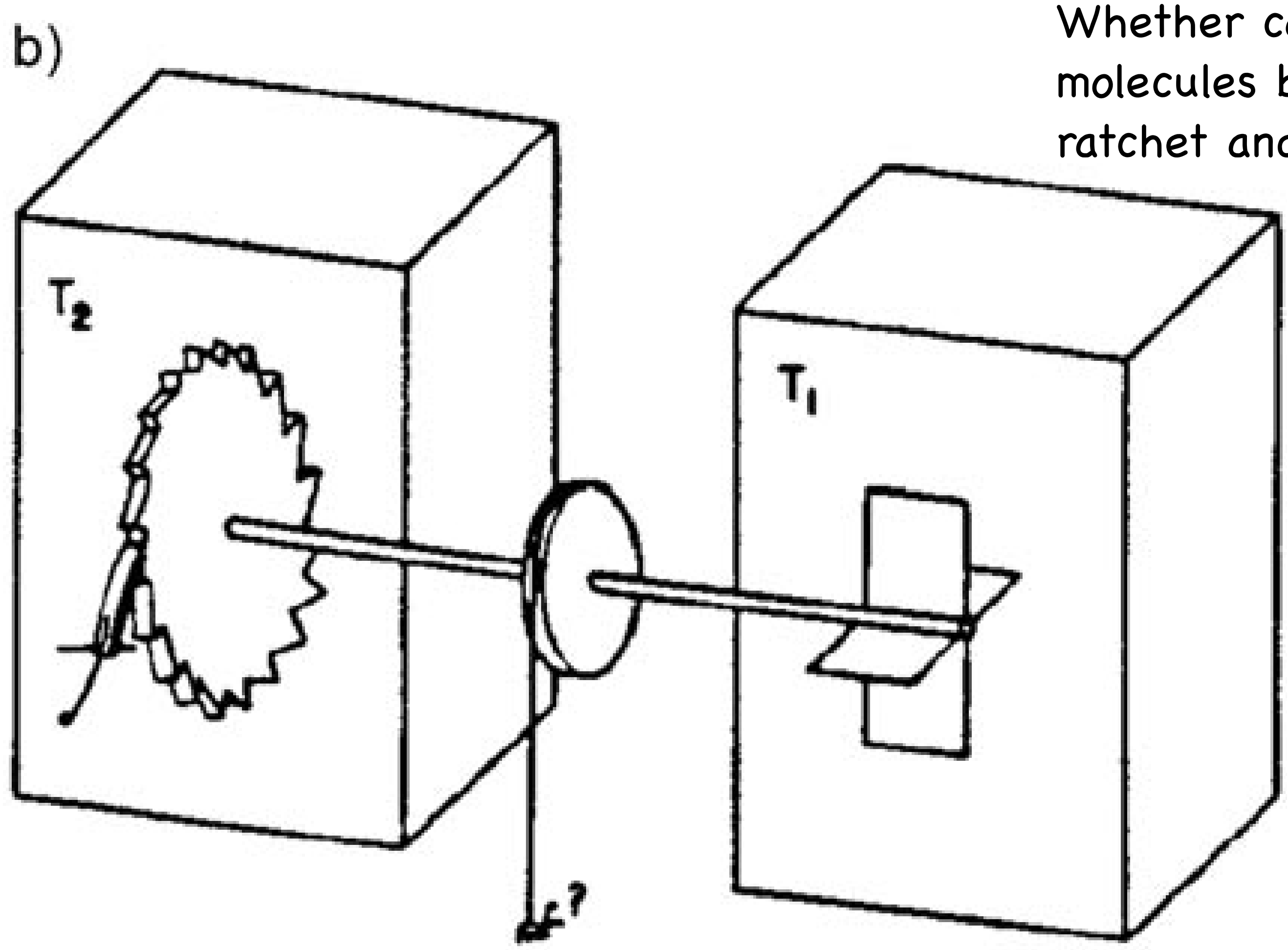
b) pressure demon

Demon works against the second law of thermodynamics.
(randomness -> direction)

D. Leigh *Angew. Chem. Int. Ed.* **2007**, *46*, 72-191

Directionality

- Feynman's Brownian Ratchet



Whether can the random oscillations produced by gas molecules bombarding the vanes be rectified by the ratchet and pawl so as to get net motion in one direction?

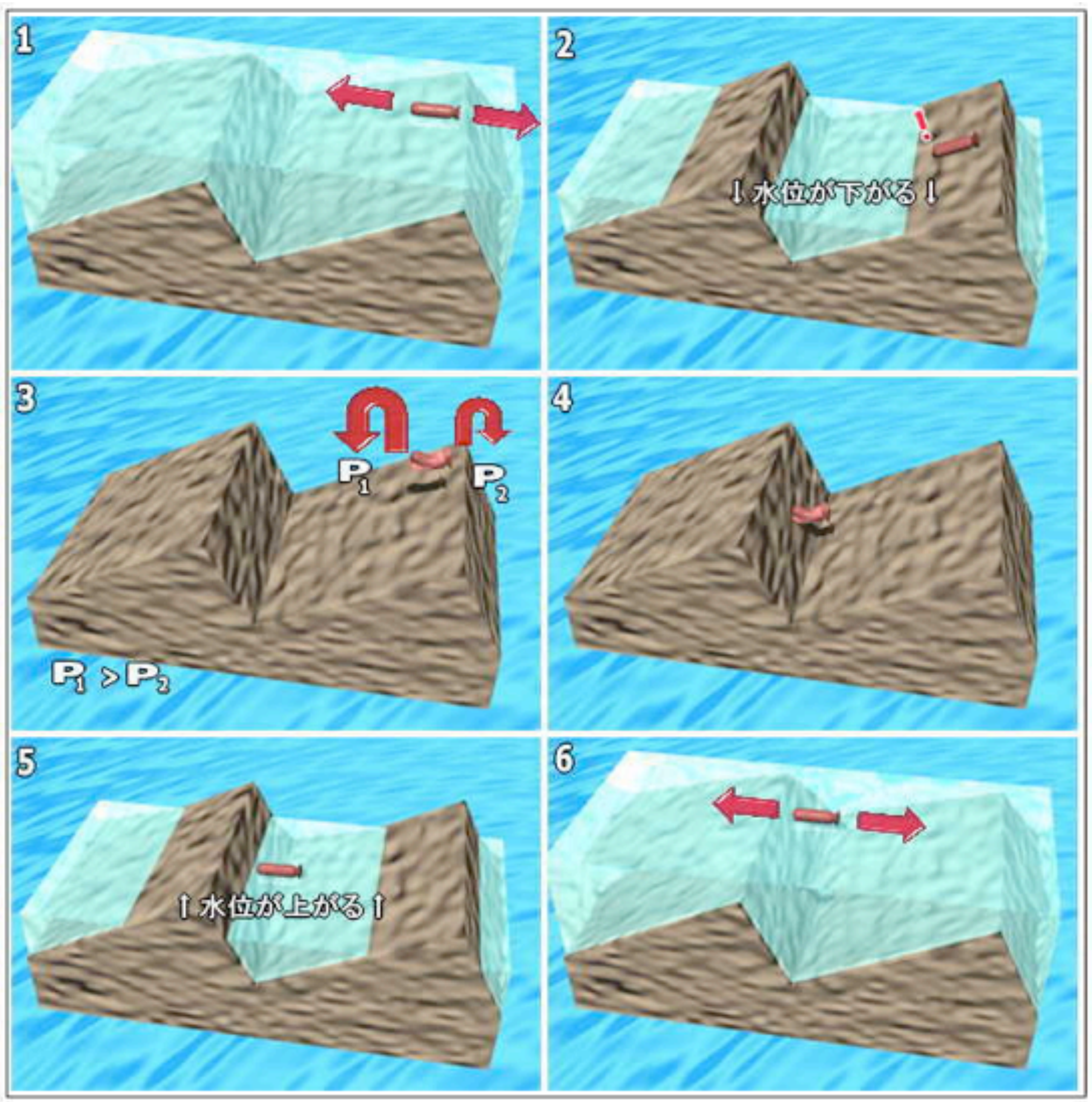
If T1 = T2, the answer is "no".

However, on the contrary, cooling the ratchet and pawl by external means makes it possible to rectify the random motion.

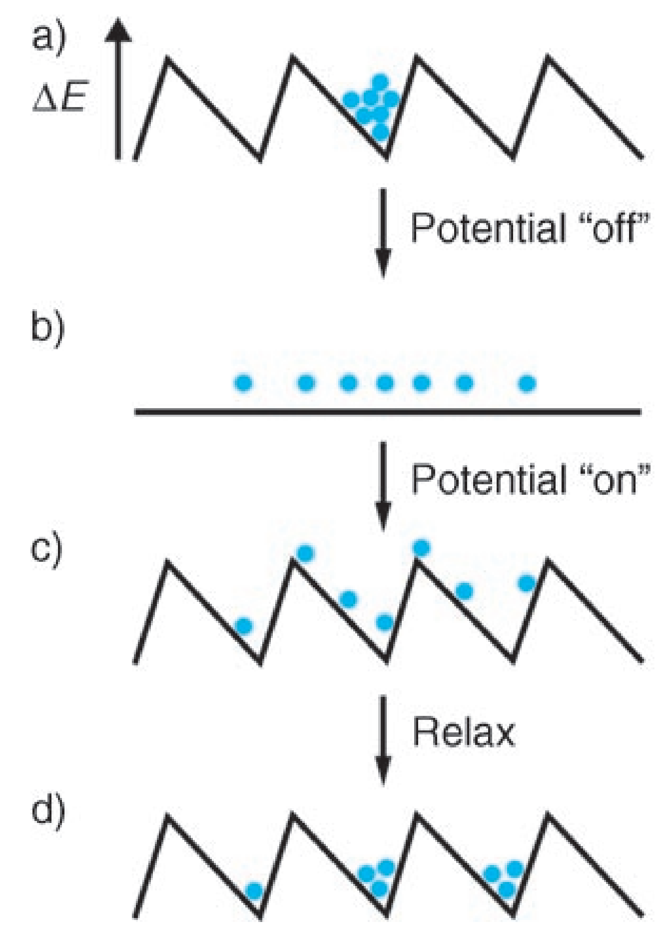
D. Leigh *Angew. Chem. Int. Ed.* **2007**, *46*, 72-191

Directionality

- Energy-ratchet



http://www.s-graphics.co.jp/tankentai/news/molecularmotor2.htm



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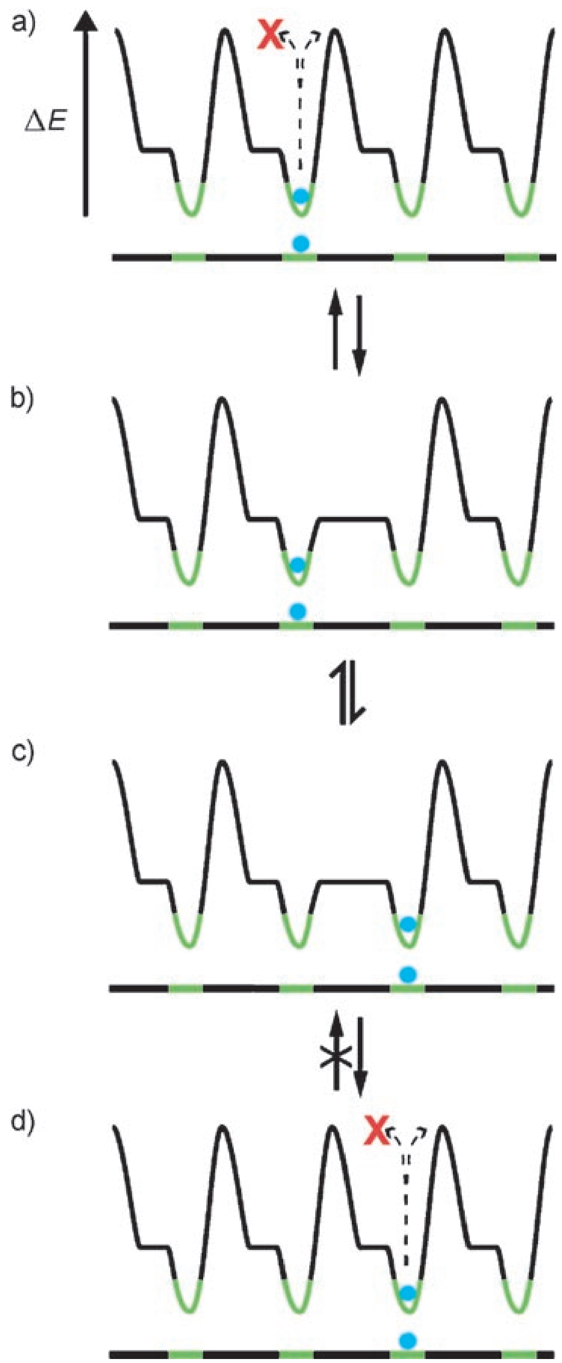
Directionality

- Information-ratchet



a) The particle starts in one of the identical-minima energy wells.

b) The position of the particle lowers the kinetic barrier.

c) The particle moves to the adjacent right-hand well by Brownian motion.

d) The particle can no longer go back to the starting well.

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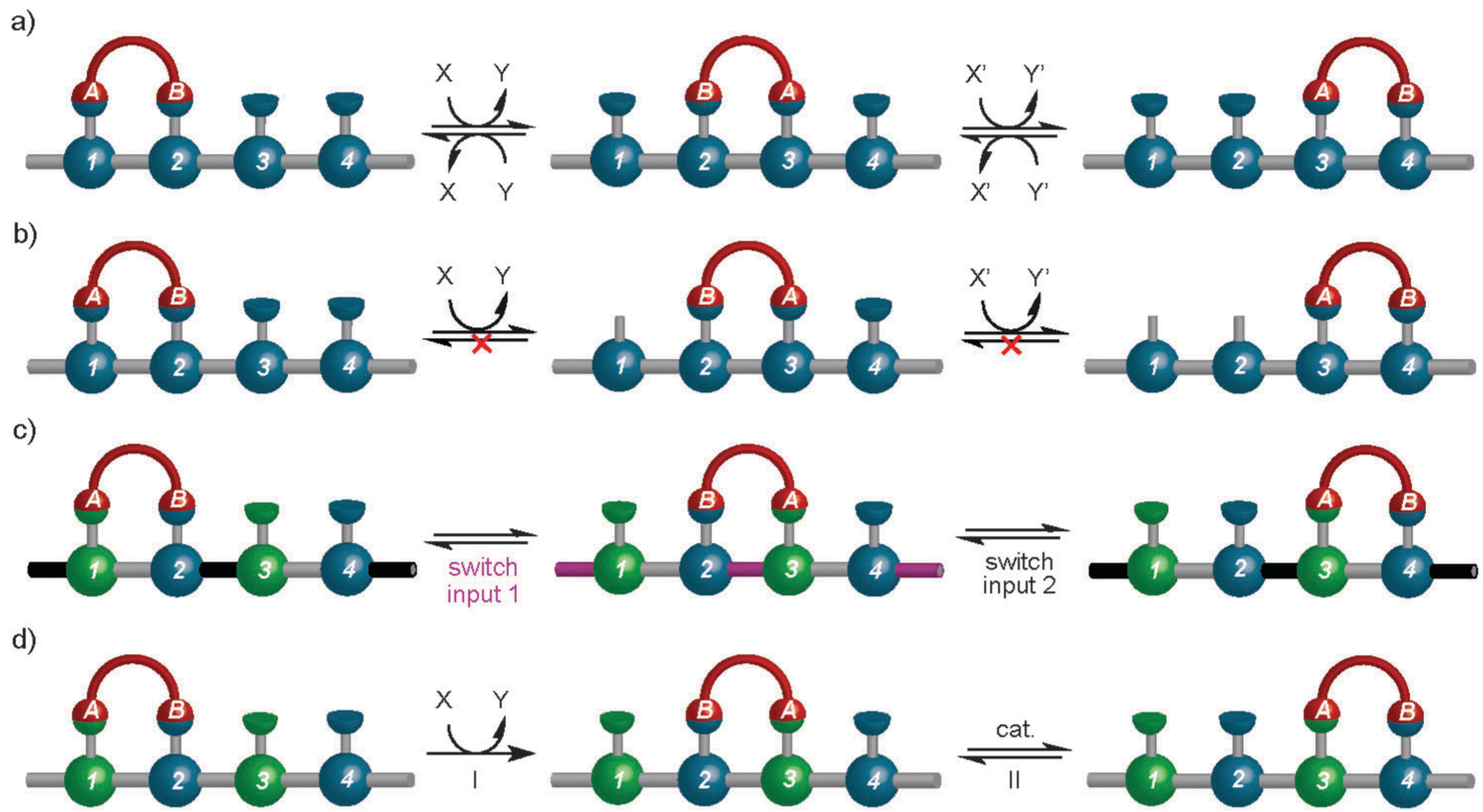
Directionality

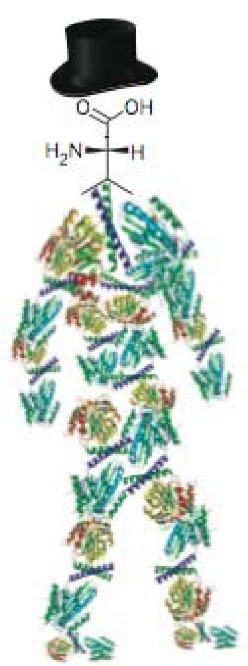
- To achieve directionality



a) reversible foot exchange
b) a "burnt-bridges" walker
c) migration requiring energy input through switching stimulus
d) irreversible, kinetically controlled migration

D. Leigh *Chem. Soc. Rev.* **2011**, ASAP

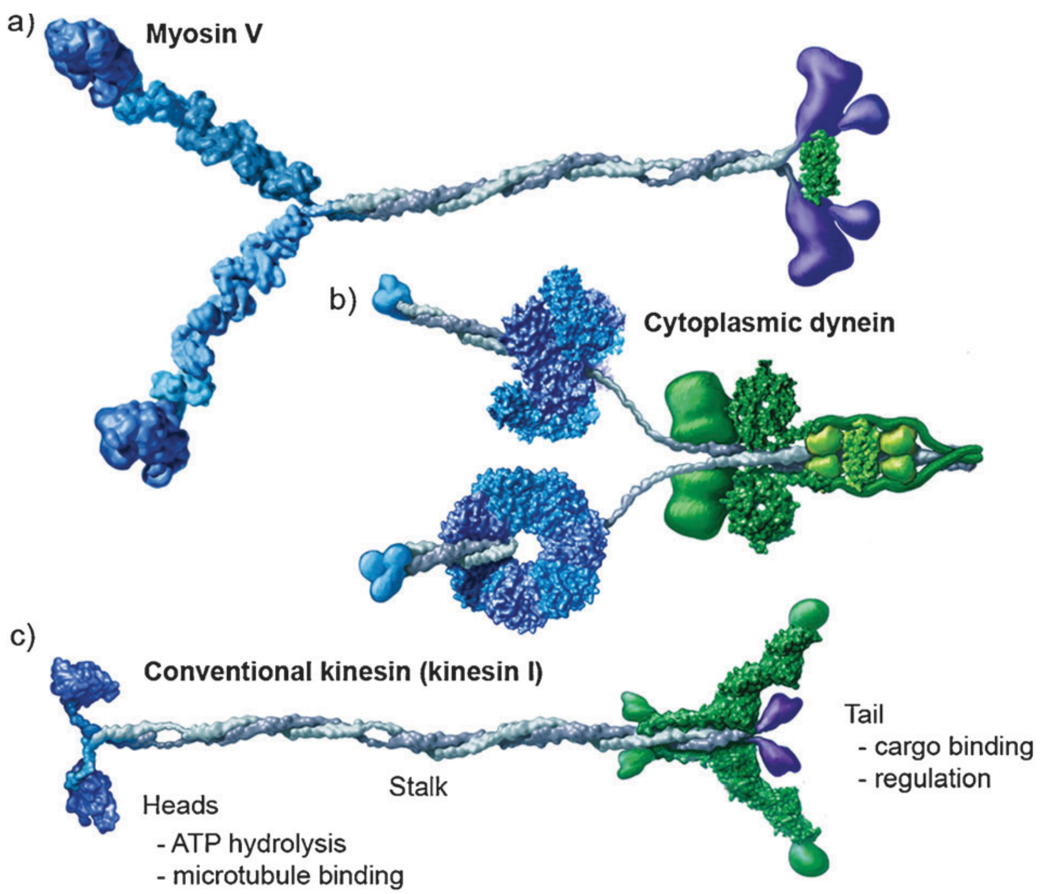
II.Biological Walker



Biological
protein walkers

Walker in Cell

- Motor Proteins



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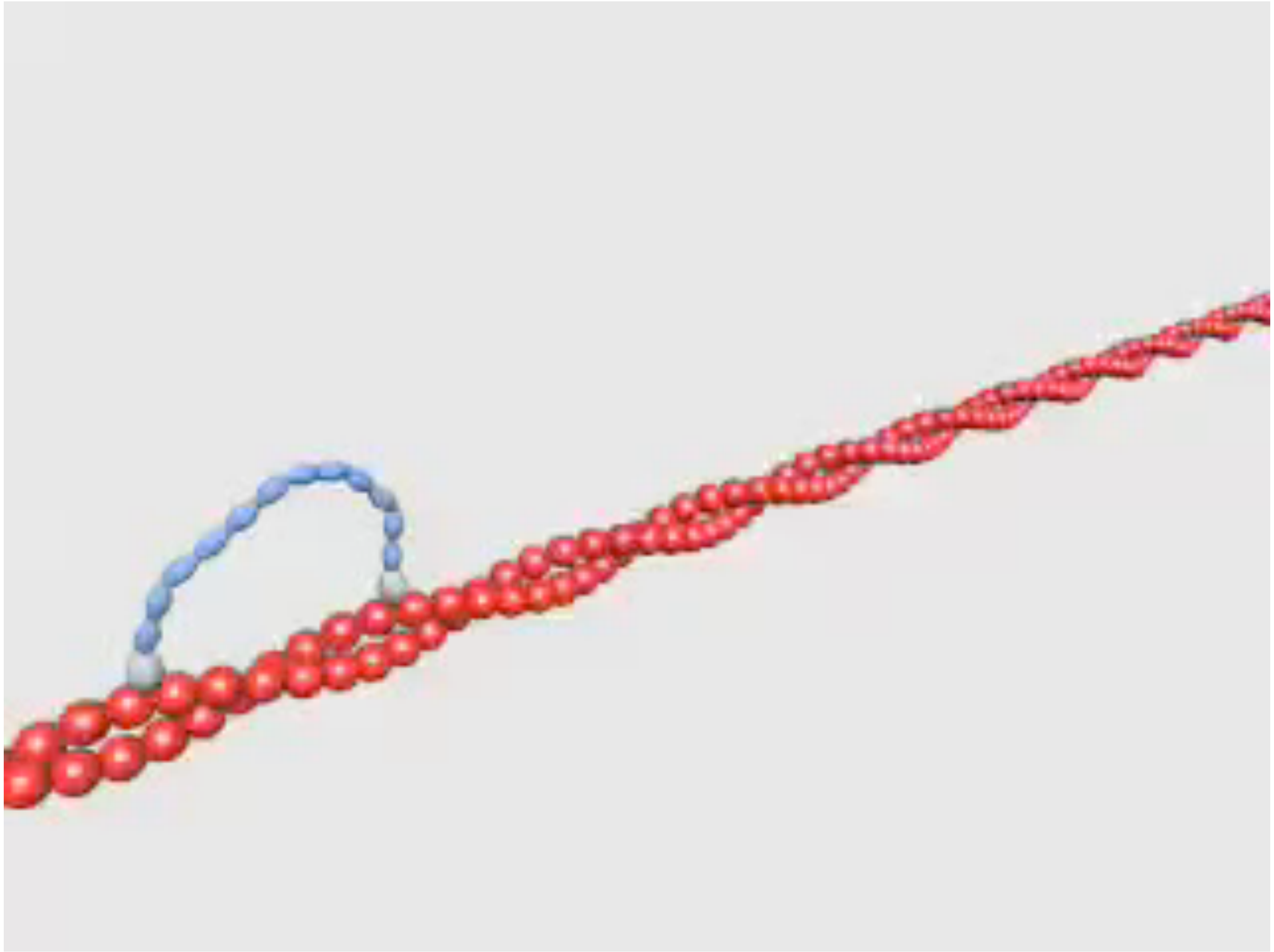
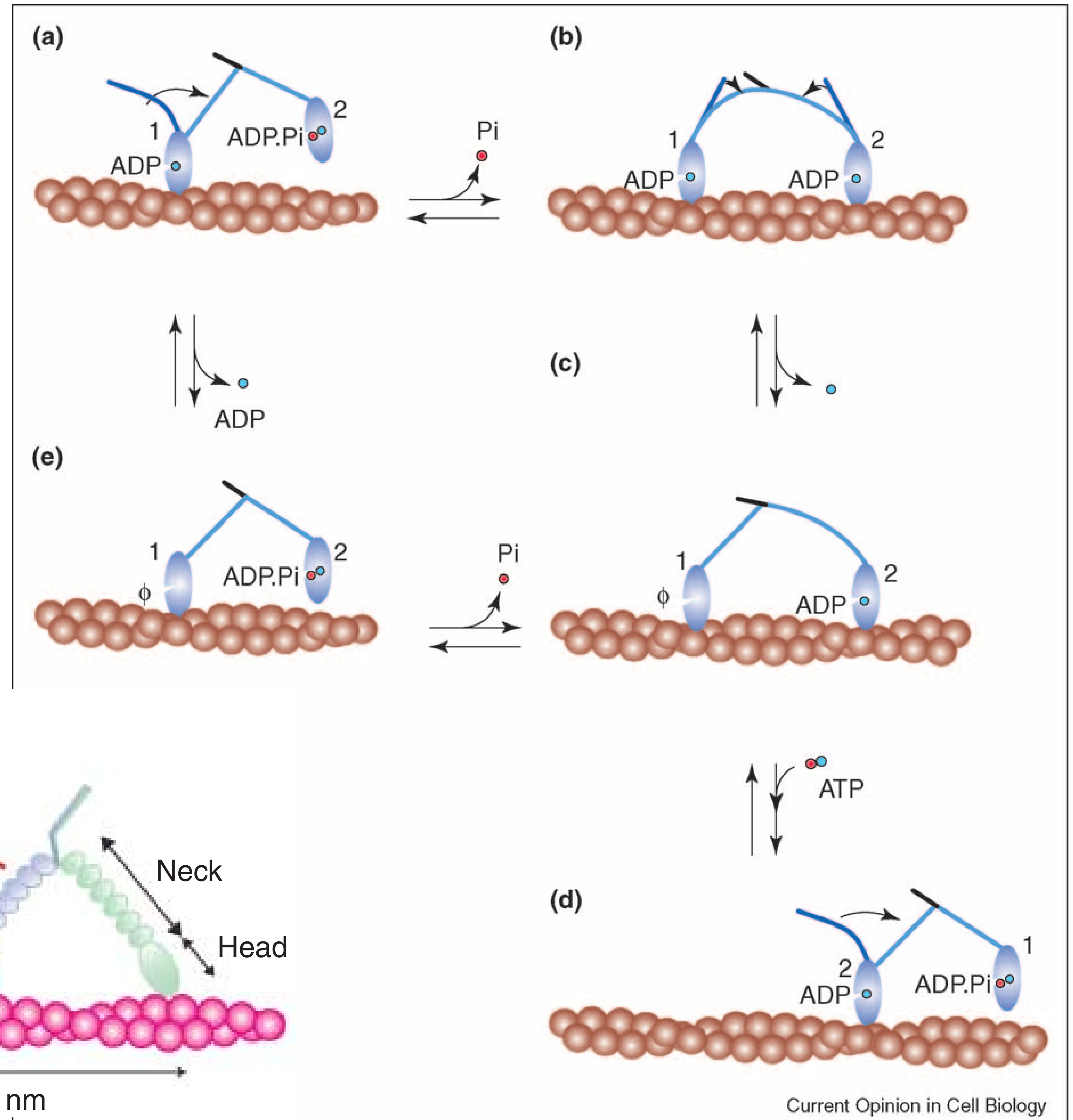
Walker in Cell

- Myosin-V



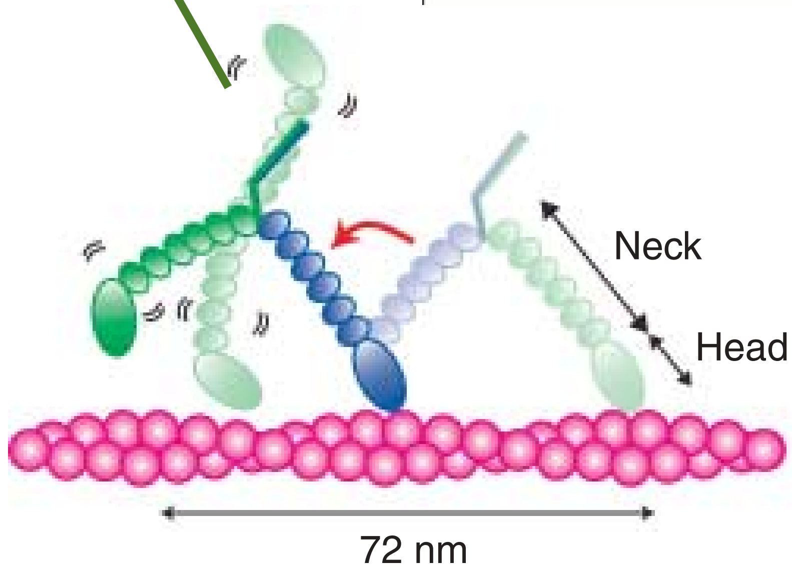
Walker in Cell

- Myosin-V



Browinan motion

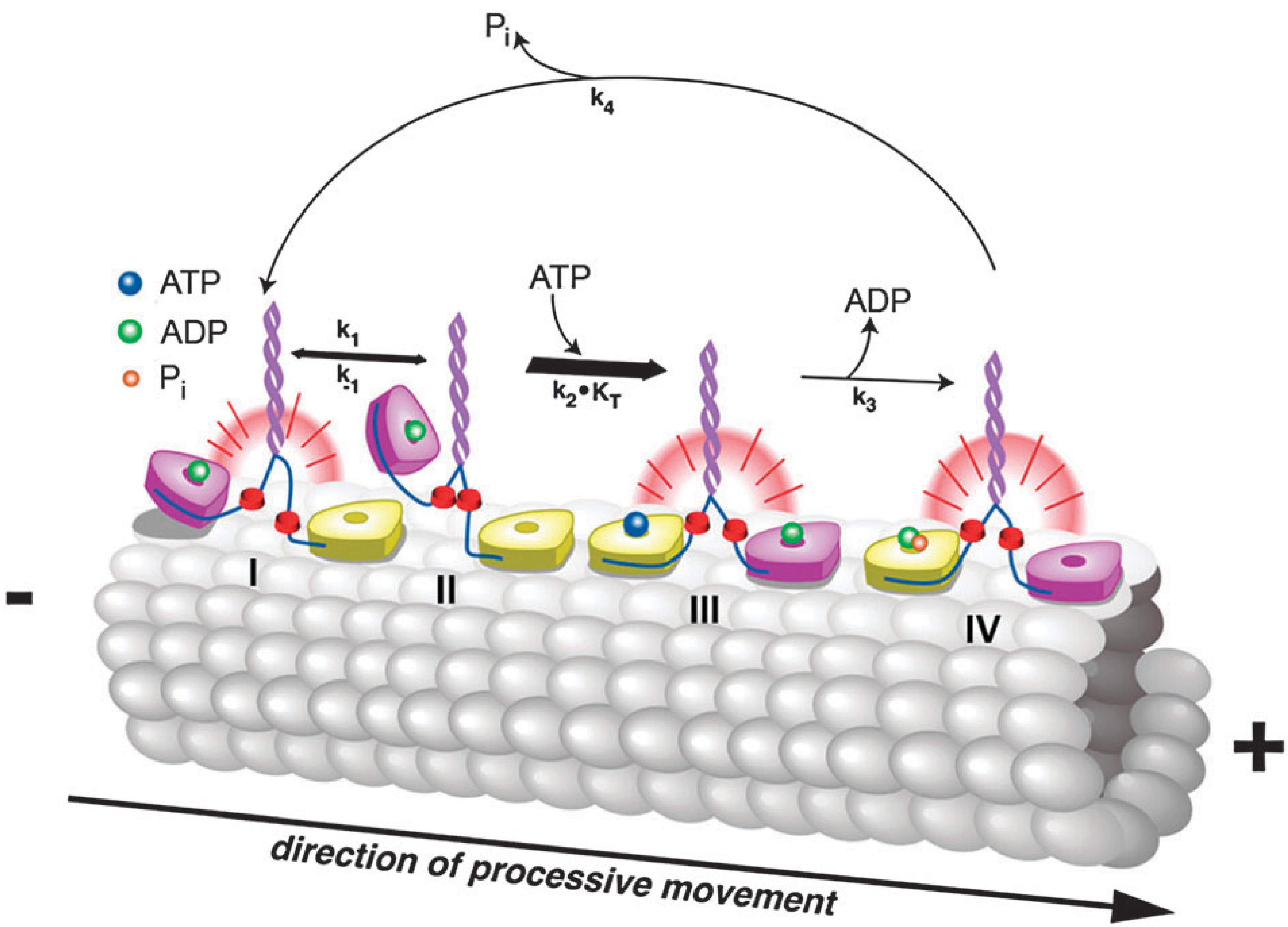
A



J. R. Sellers *Curr. Opin. Cell Biol.* **2006**, *18*, 68; K. Kinoshita *Science*, **2007**, *316*, 208

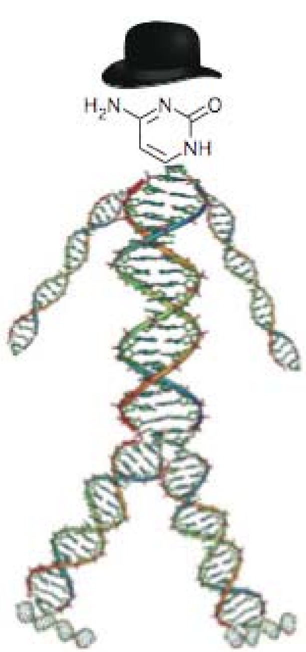
Walker in Cell

- Kinesin-I



P.R.Selvin *Proc. Natl. Acad. Sci. U. S. A.* **2009**, *106*, 12717

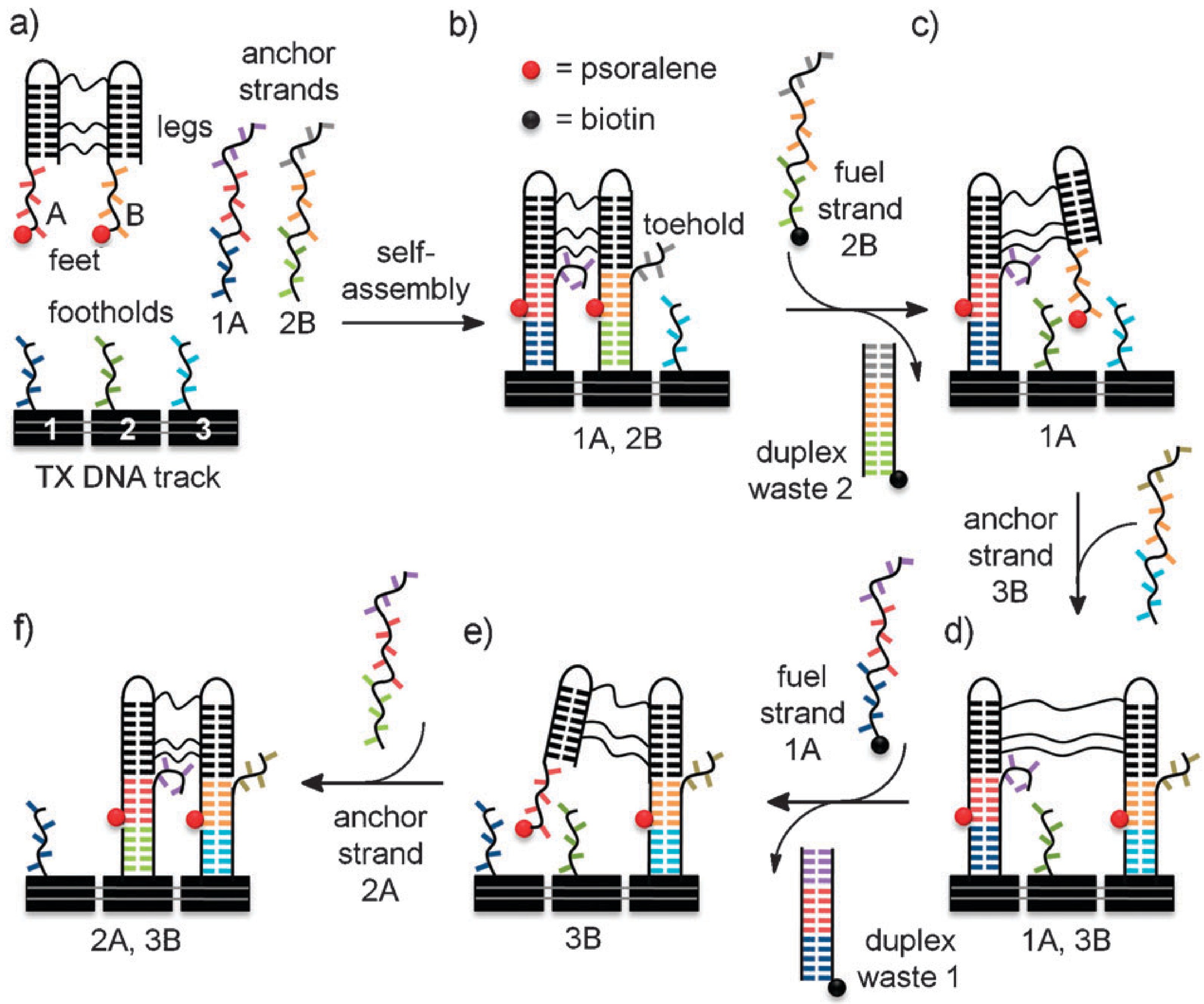
III.DNA Walker



Artificial
DNA walkers

DNA Walker

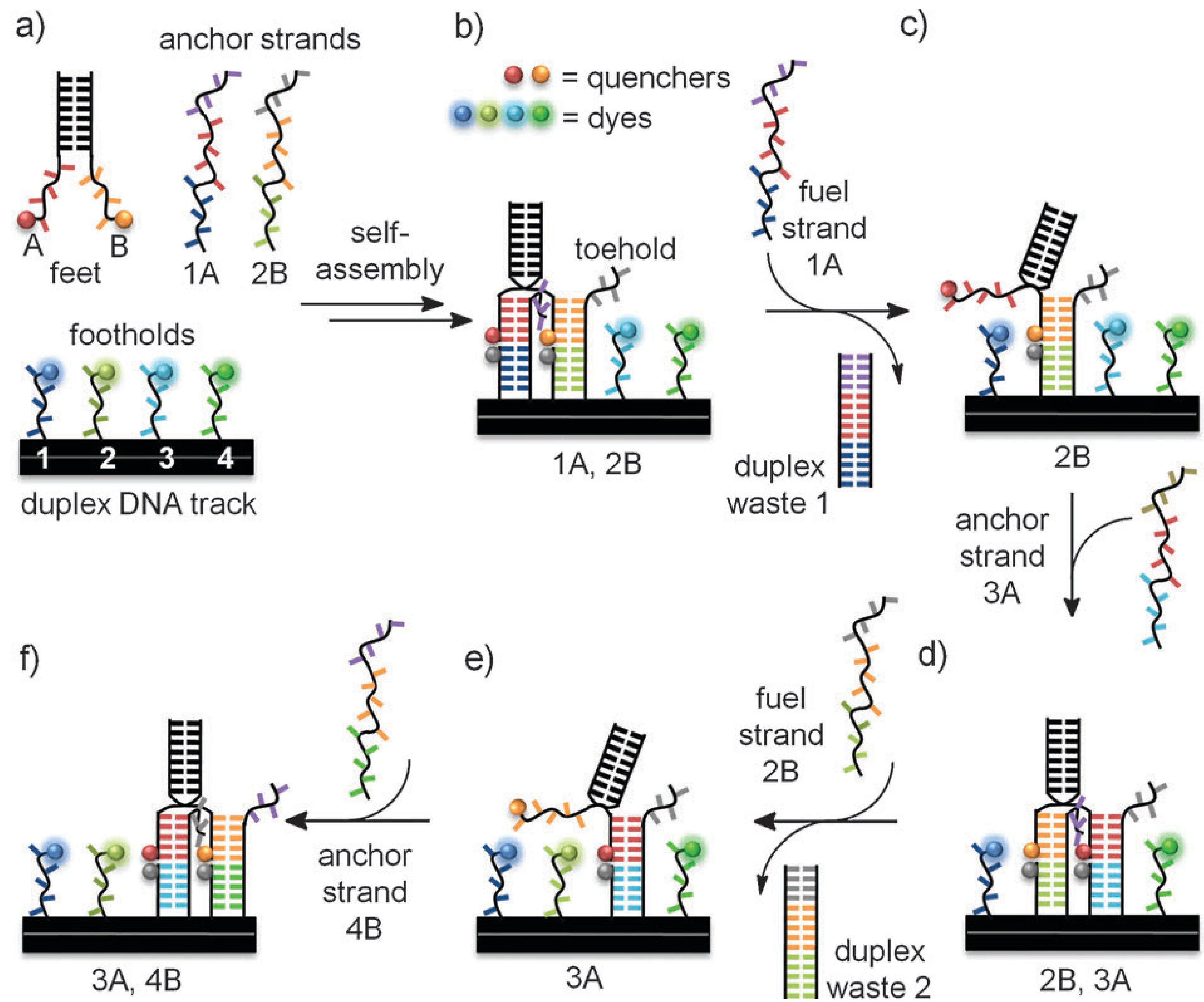
- Non-autonomous DNA Walker



N. C. Seeman *Nano Lett.* **2004**, *4*, 1203

DNA Walker

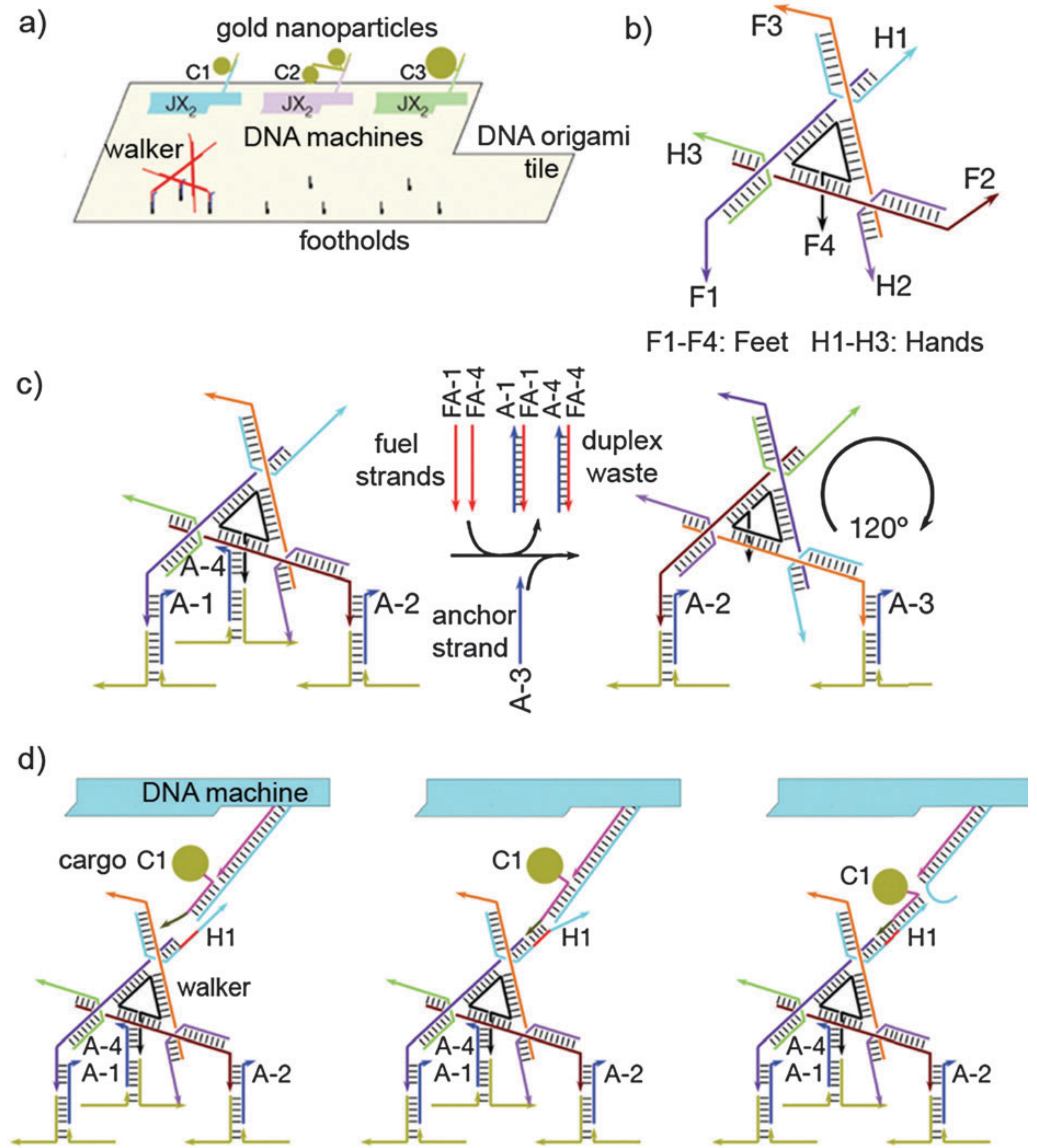
- Non-autonomous DNA Walker



N. A. Pierce *J. Am. Chem. Soc.* **2004**, *126*, 10834

DNA Walker

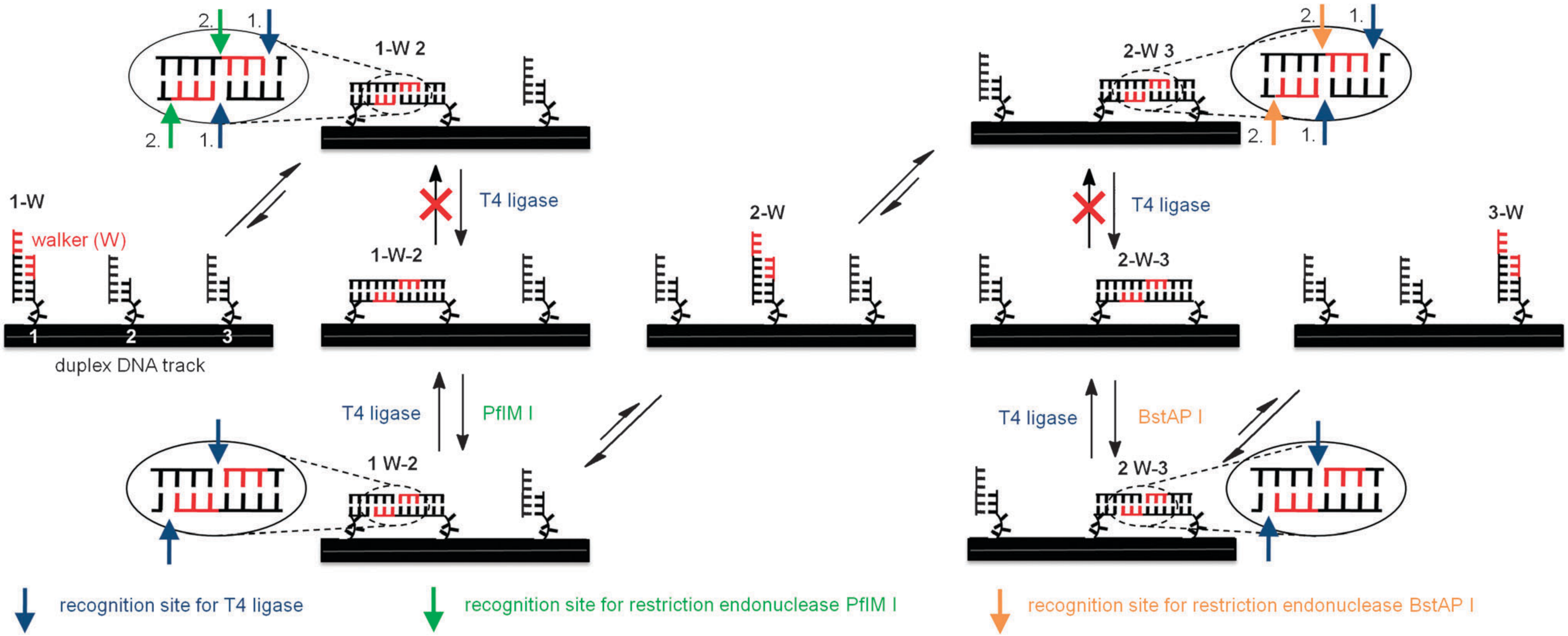
- Two-dimensional Walker



N. C. Seeman *Nature* **2010**, *465*, 202

DNA Walker

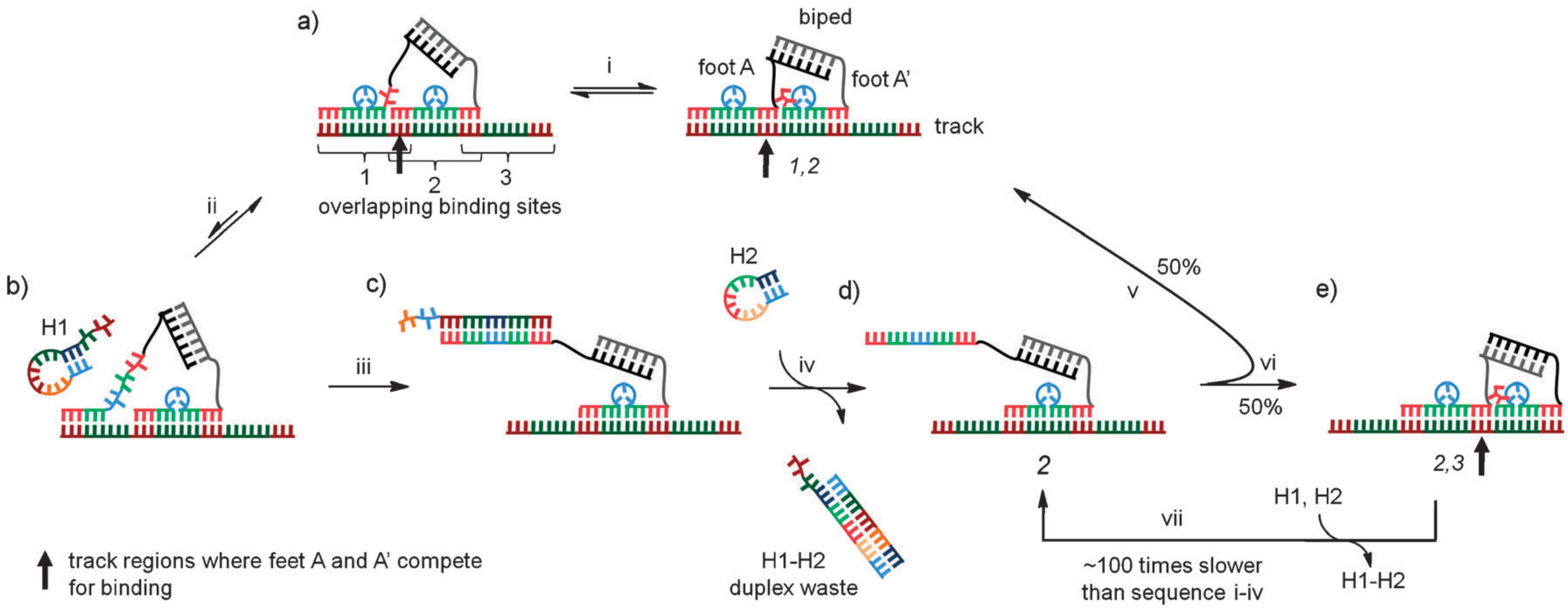
- Autonomous DNA Walker



A. J. Turberfield *Angew. Chem. Int. Ed.* **2004**, *43*, 4906

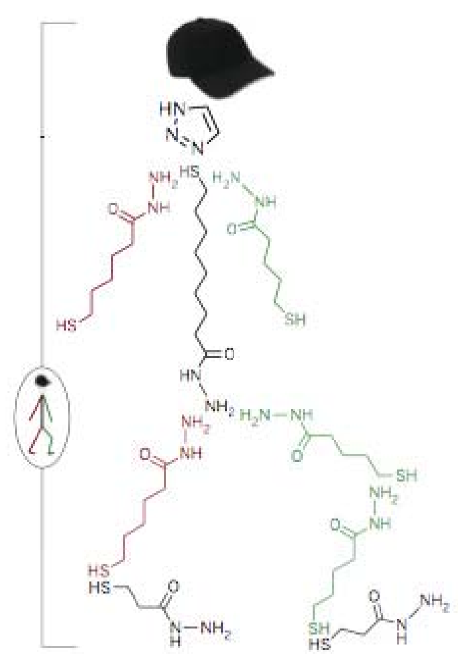
DNA Walker

- Autonomous DNA Walker



A. J. Turberfield *Phys. Rev. Lett.* **2008**, *101*, 238101

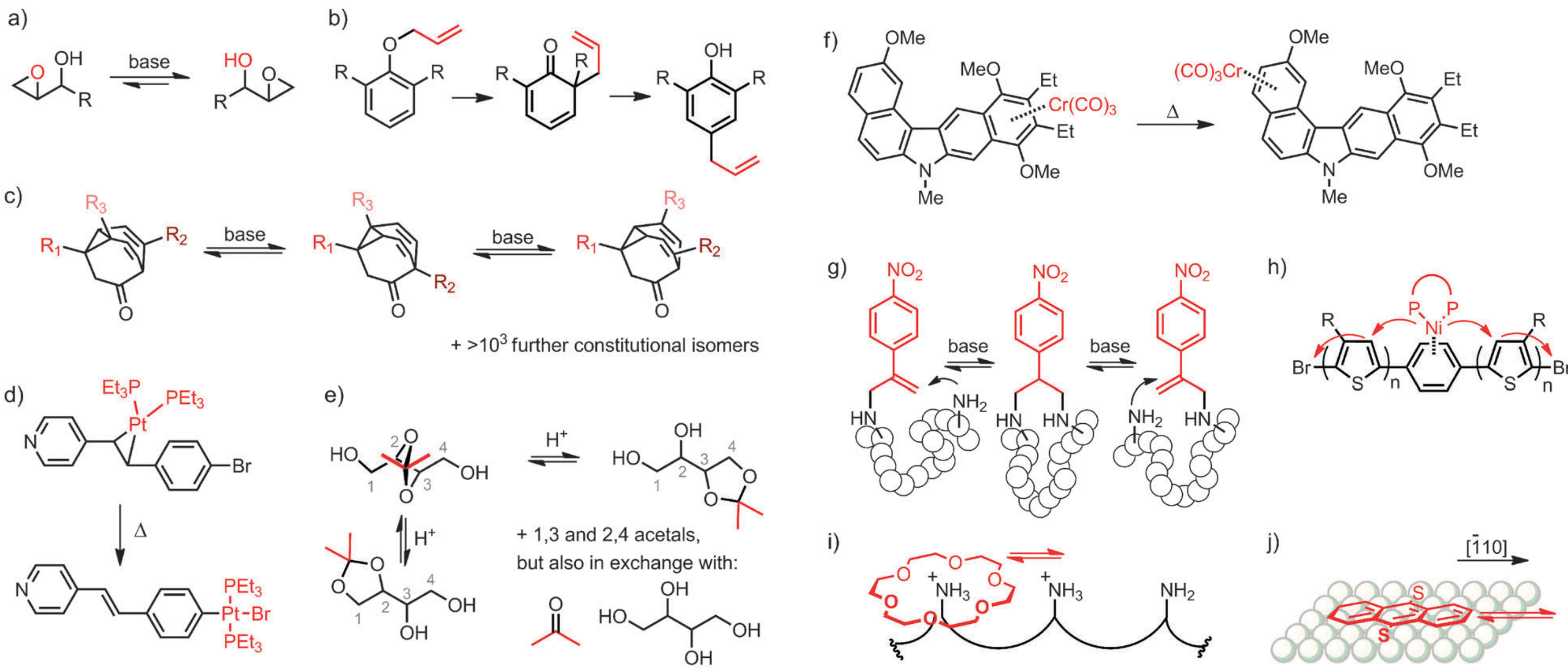
IV.Small-molecule Walker



Artificial
small-molecule walkers

Walking Small Molecule

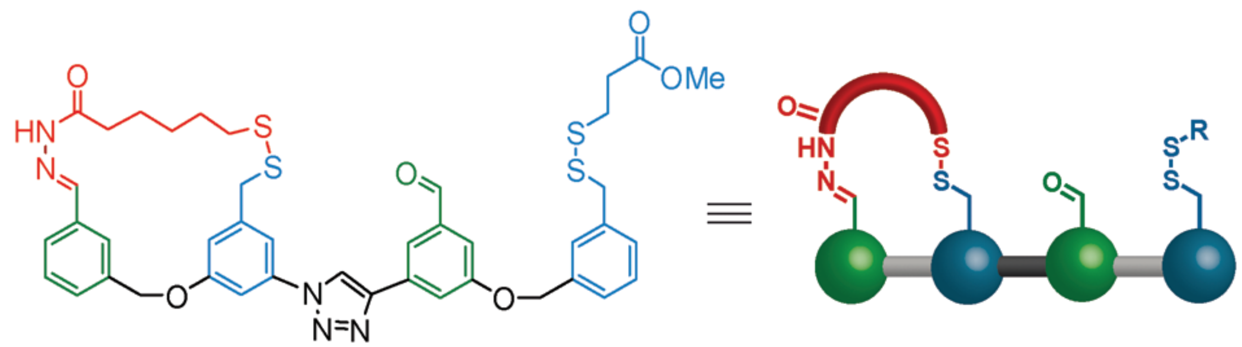
- Migration of small molecule fragments



D. Leigh *Chem. Soc. Rev.* **2011**, ASAP

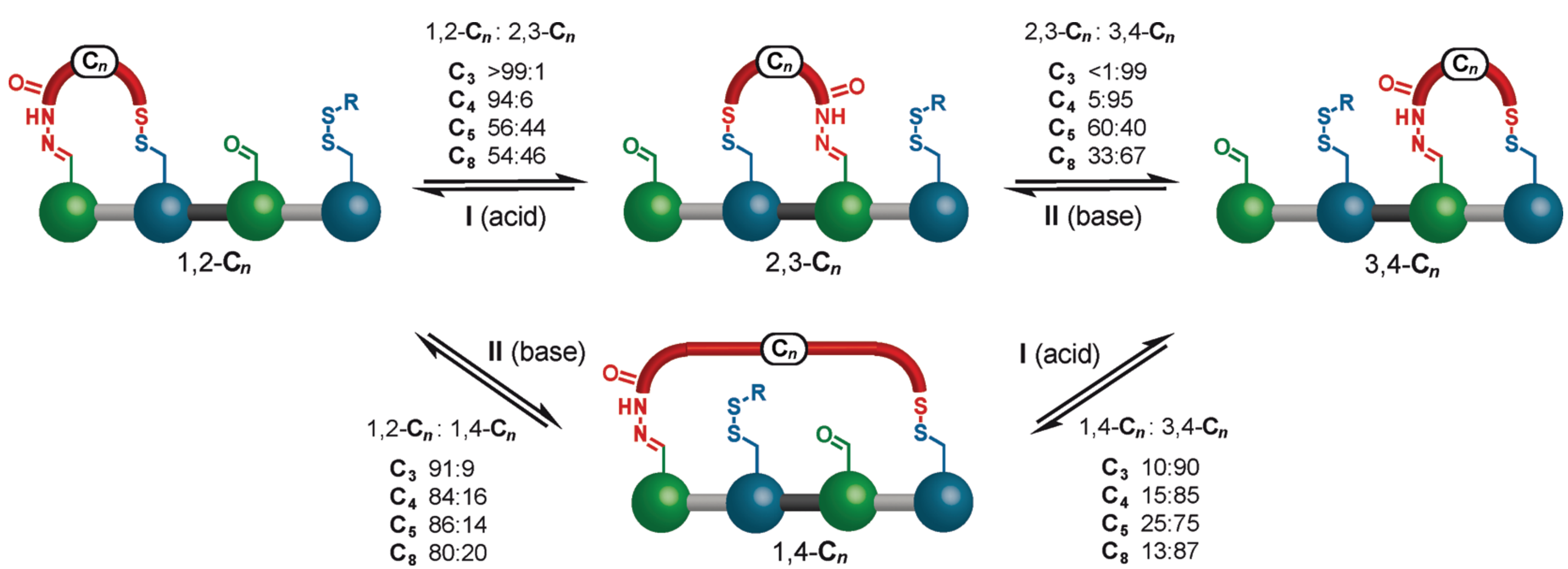
Walking Small Molecule

- Synthetic Walker



1,2-$\mathbf{C_5}$

Synthesized small molecule walker

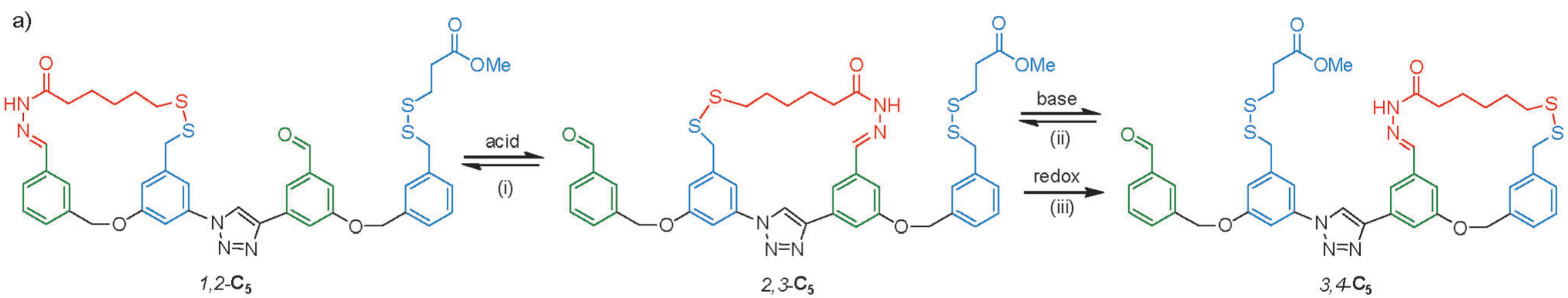


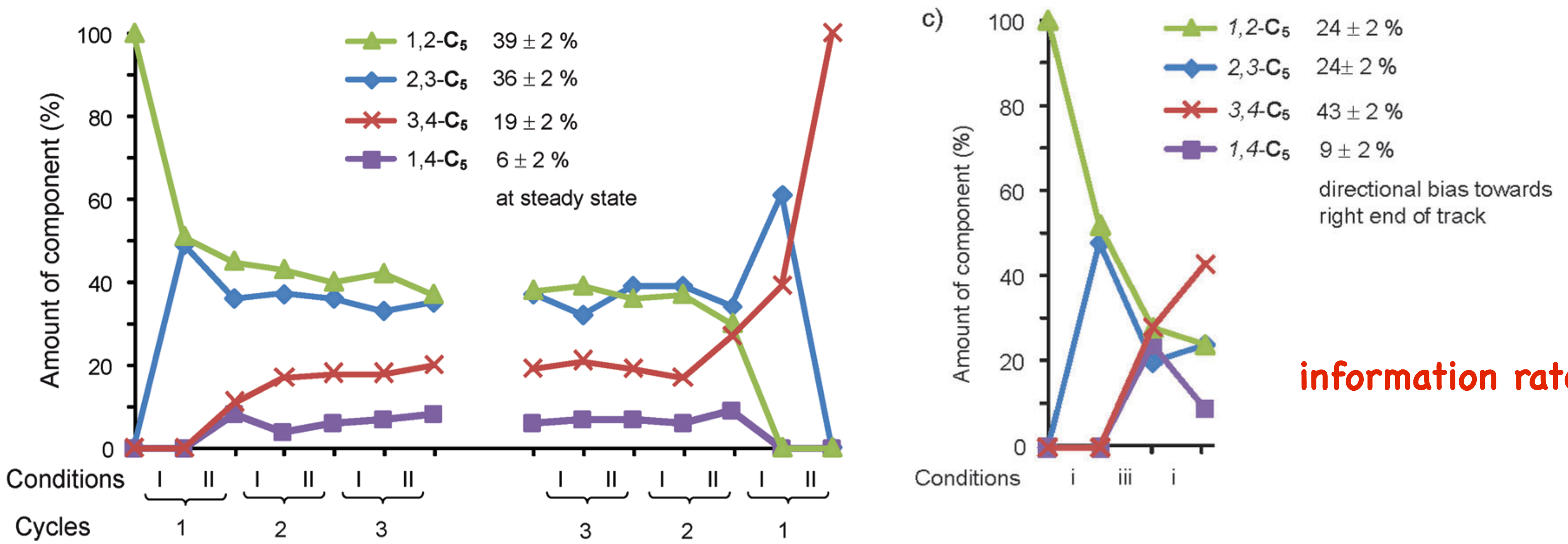
Reversible reactions that connect various pairs of the positional isomers

D. Leigh *J. Am. Chem. Soc.* **2010**, *132*, 16134

Walking Small Molecule

- Distribution of the walker





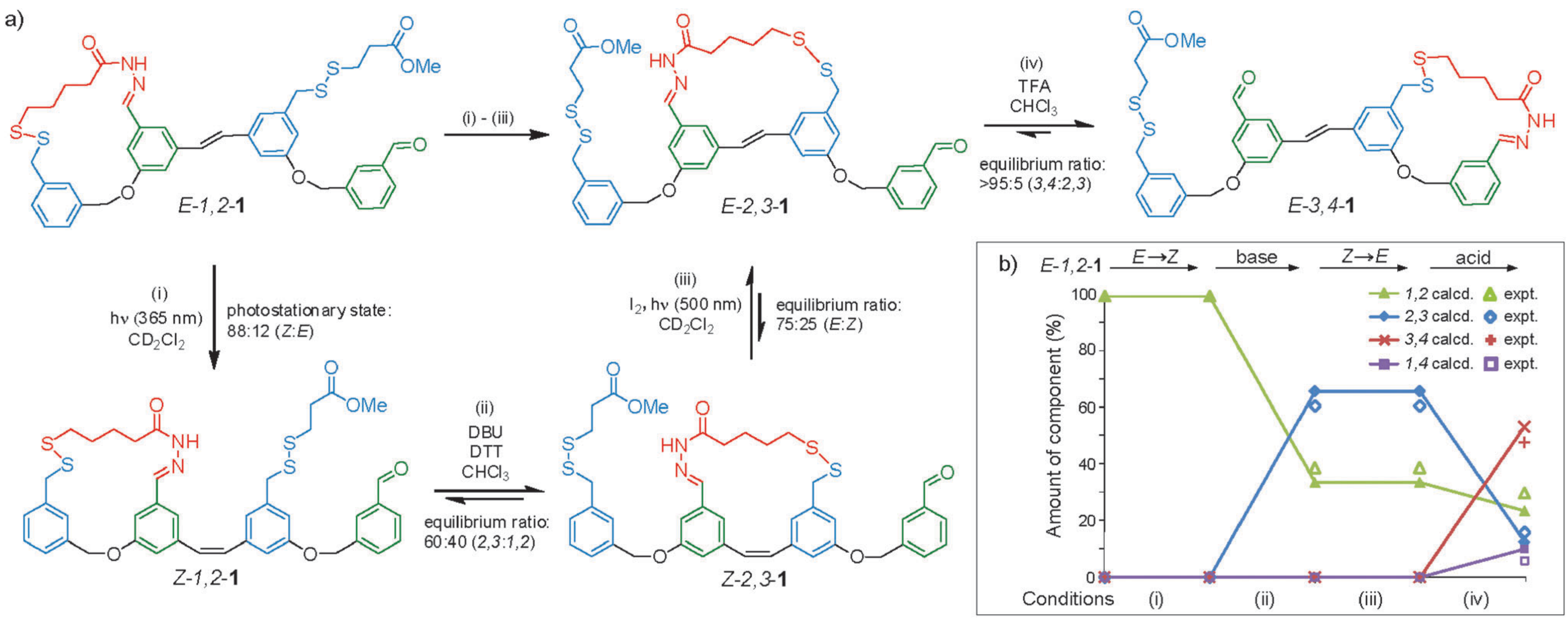
information ratchet

conditions : (i) 0.1mM, TFA, $CHCl_3$, rt (ii) 0.1mM, DTT(10eq), DBU(40eq), dimethyl 3,3'-disulfanediyldipropionate(20eq), $CHCl_3$, rt (iii) a. 1.0mM, DTT(6eq), DBU(3eq), $CDCl_3$, reflux; b. 0.1mM, Et_3N(xs), methyl 3-mercaptopropionate(8eq), I_2 (12eq), $CDCl_3$/MeOH, rt

D. Leigh *J. Am. Chem. Soc.* **2010**, *132*, 16134

Walking Small Molecule

- Light-driven small-molecule walker



energy ratchet

D. Leigh *Angew. Chem. Int. Ed.* **2011**, *50*, 285

V. Summary

Walking Molecules

- Difference between respective walkers

Biological
- efficient
- need ATP as fuel
- only in aqueous environment
- modest stability

DNA
- automated synthesize
- designed by a computer
- complex tracks(DNA origami)
- need DNA as fuel

Small-molecule
- small size
- low efficient
- more stable
- in various environments
- not need ATP

Walking Molecules

- What is a role of "walker"?

Walker is employed for driving chemical systems away from **equilibrium**.

Life is or isn't a complex system of **equilibrium**.

a new chemical system mimicking life