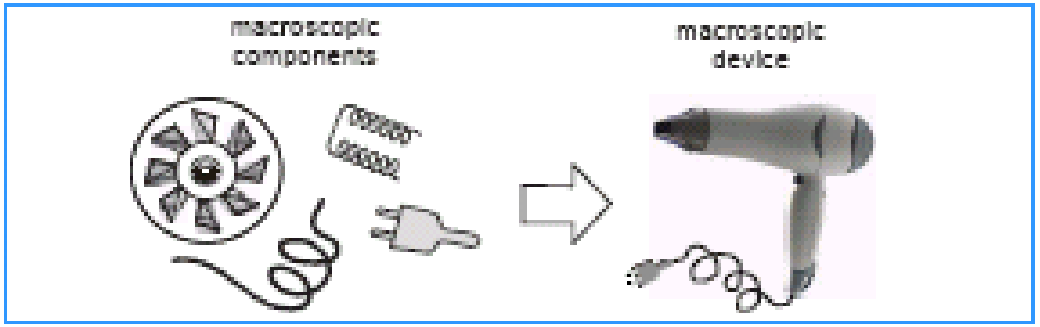
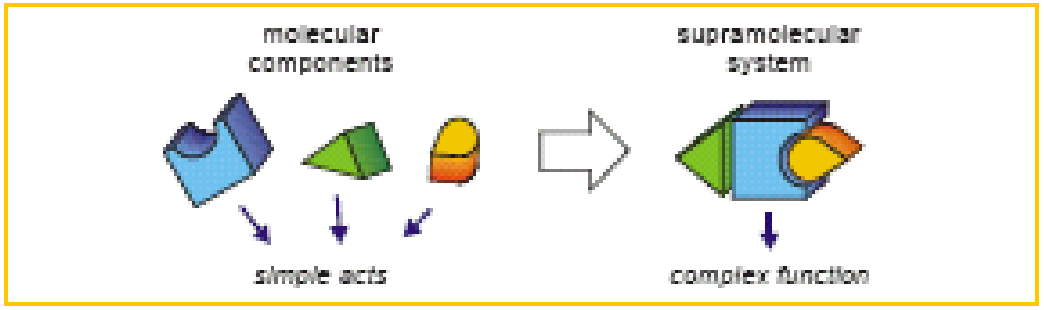
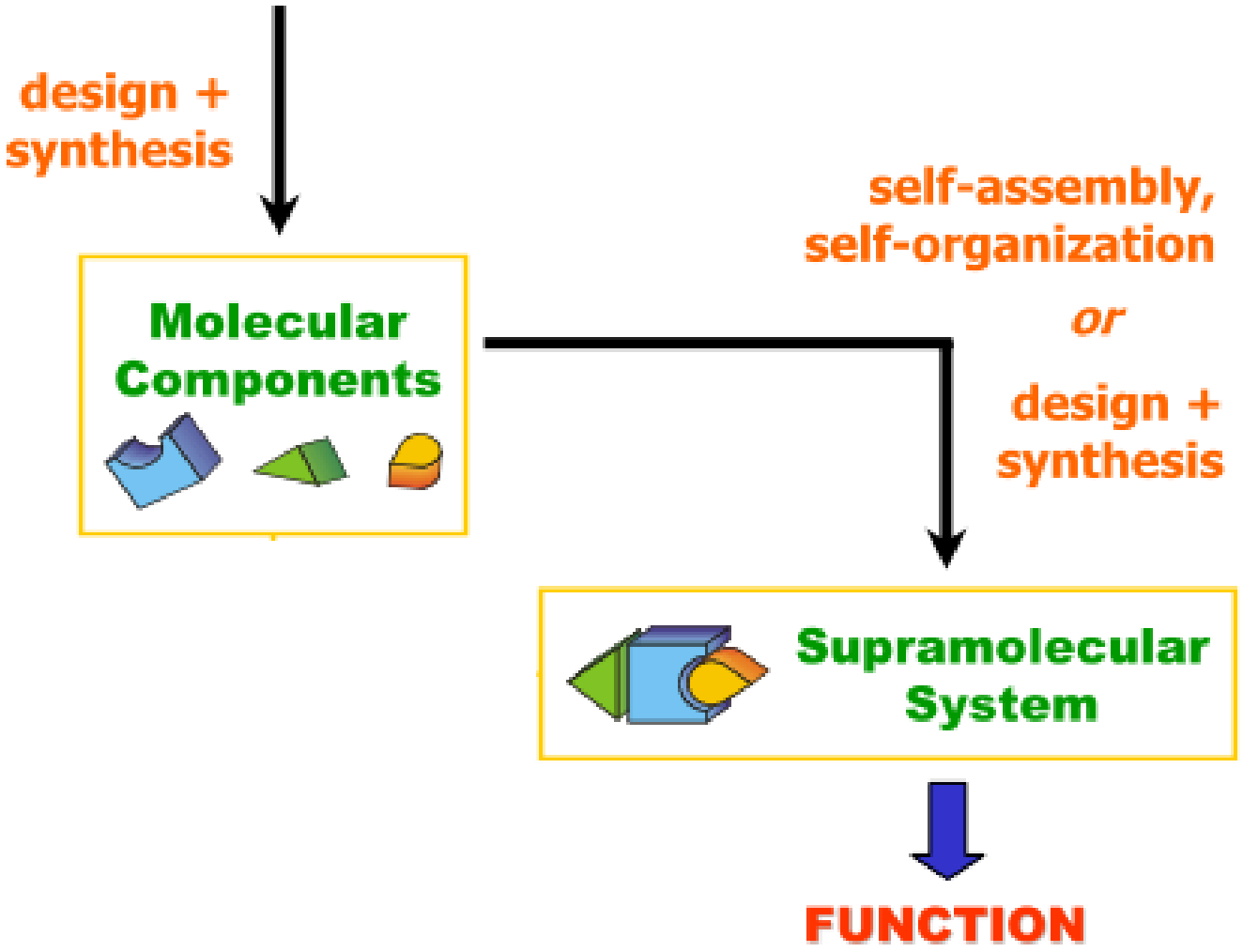
Dispositivi e Macchine Molecolari

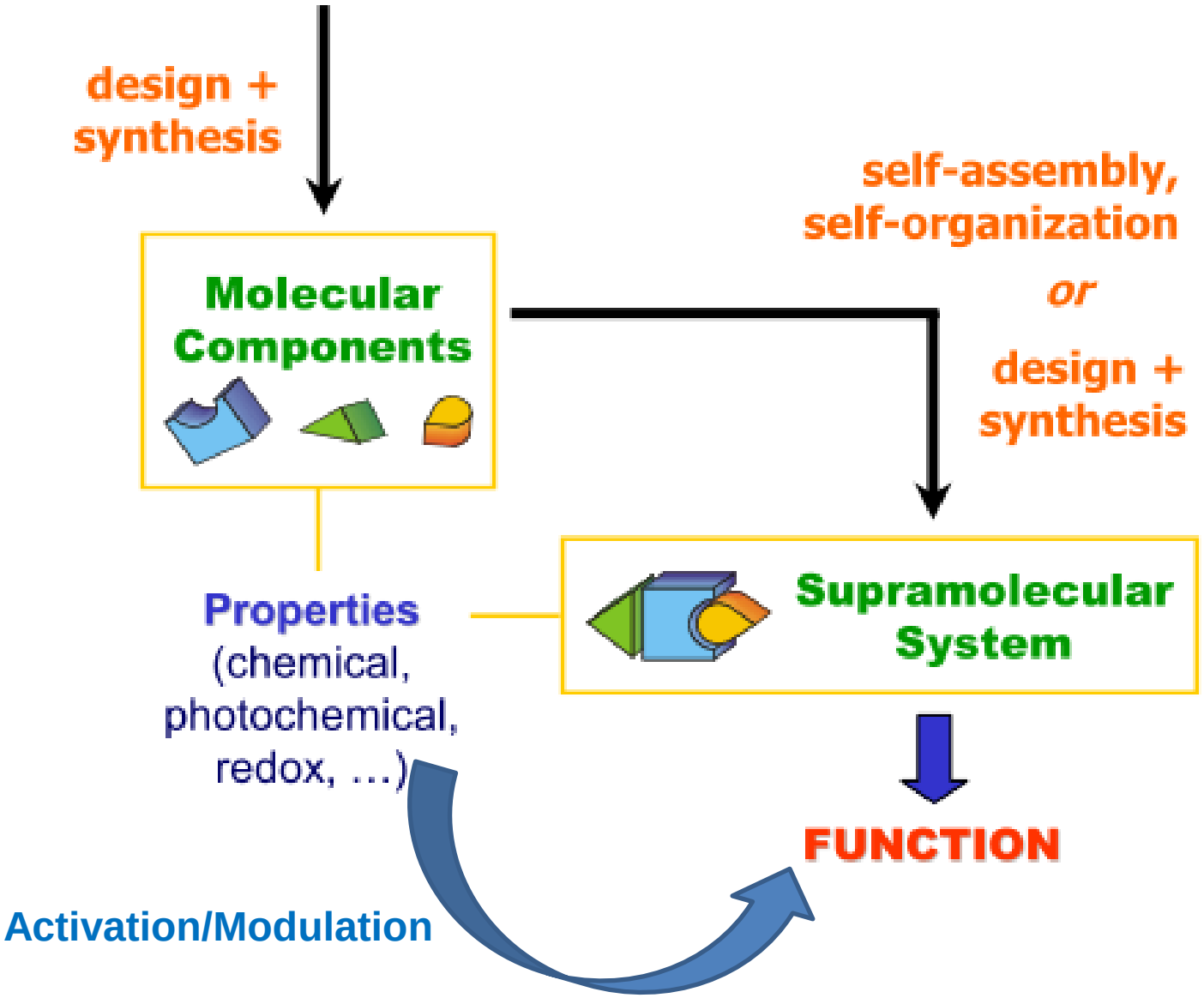
Macroscopic device



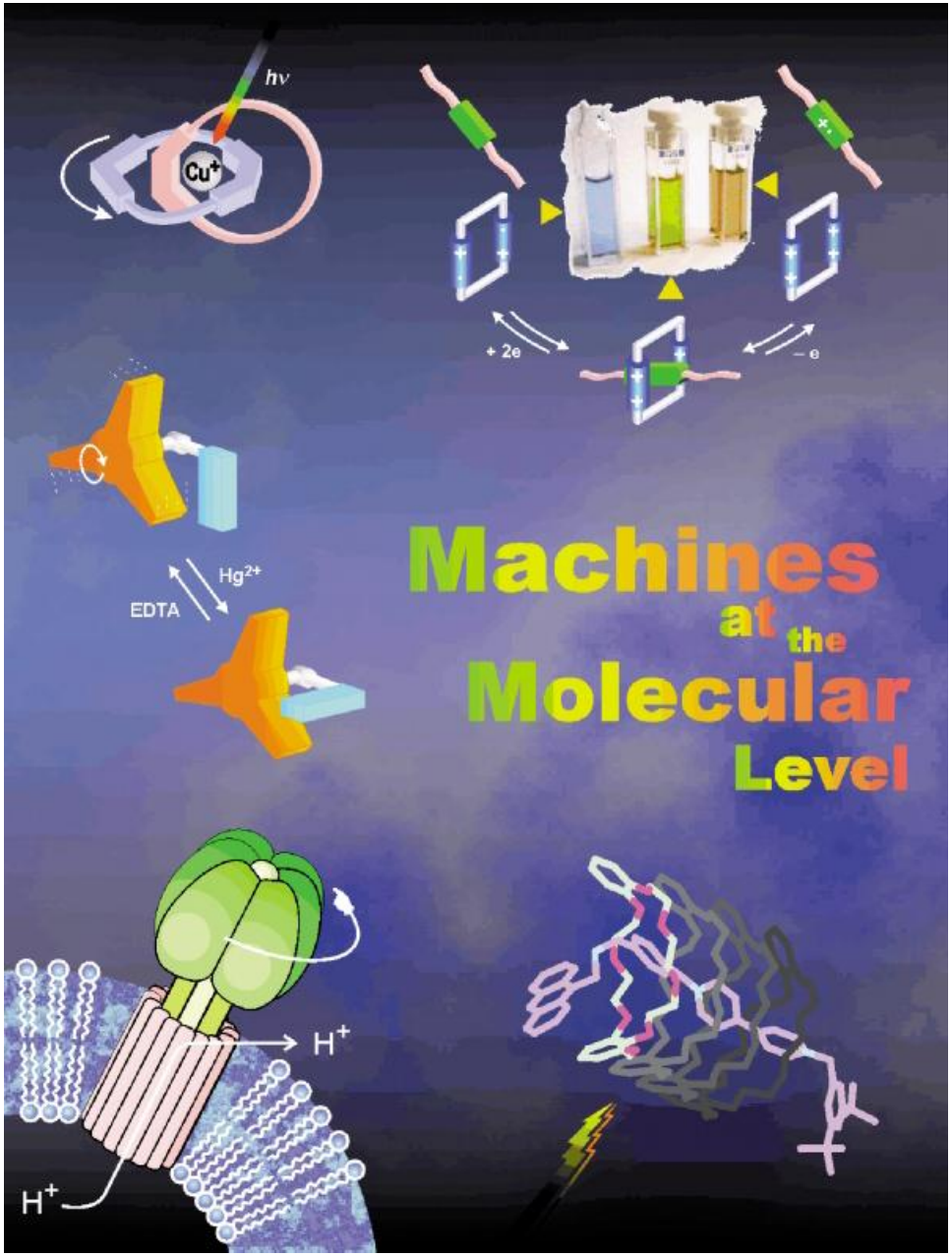
Molecular-level device




design +
synthesis
Molecular
Components
self-assembly,
self-organization
or
design +
synthesis
Supramolecular
System
FUNCTION


design +
synthesis
Molecular
Components
self-assembly,
self-organization
or
design +
synthesis
Supramolecular
System
Properties
(chemical,
photochemical,
redox, …)
FUNCTION
Activation/Modulation

- tipo di energia (chimica, fotoni, elettroni)
- monitoraggio (tecniche fotofisiche, elettrochimiche)
- processo ciclico
- tempo (picosecondi-minuti)
- funzione


hν
Cu+
+ 2e
– e
EDTA
Hg2+
H+
H+
Machines
at the
Molecular
Level

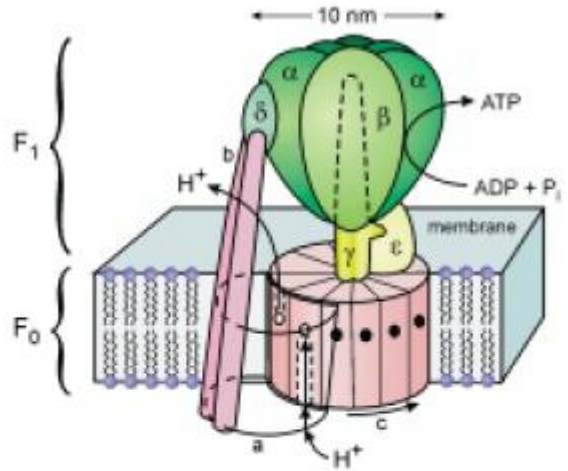


Figure 1. The structure of F_0F_1ATP synthase.[18] The catalytic region is composed of the subunits $\alpha-\varepsilon$. The proton channels lie at the interface between the subunits a and c (dashed lines indicate the putative inlet and outlet channels). Proton flow through the channels develops torque between the a and c subunits. This torque is transmitted to F_1 via the γ shaft and the ε subunit, where it is used to release ATP sequentially from the catalytic sites in F_1. The c subunit consists of 9–12 twin α-helices arranged in a central membrane-spanning array. The a subunit consists of 5–7 membrane-spanning α-helices and is connected to F_1 by the b and δ subunits. Reprinted by permission from ref. [16f] (Copyright© Macmillan Magazines Ltd 1998).

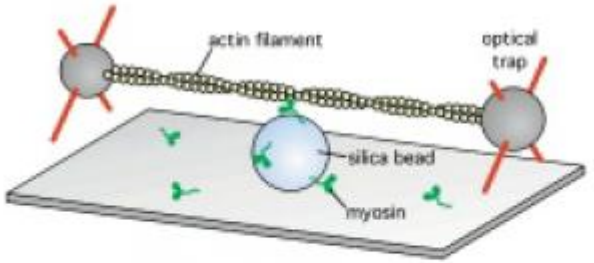
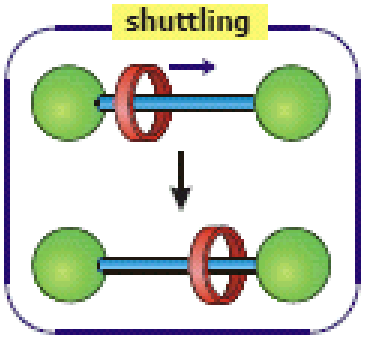
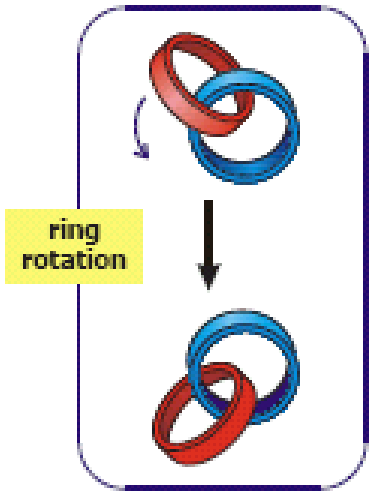
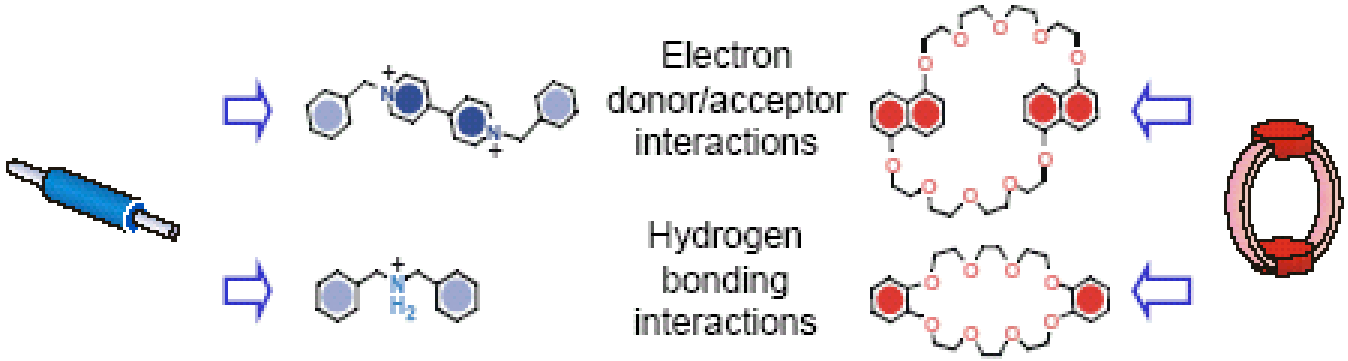


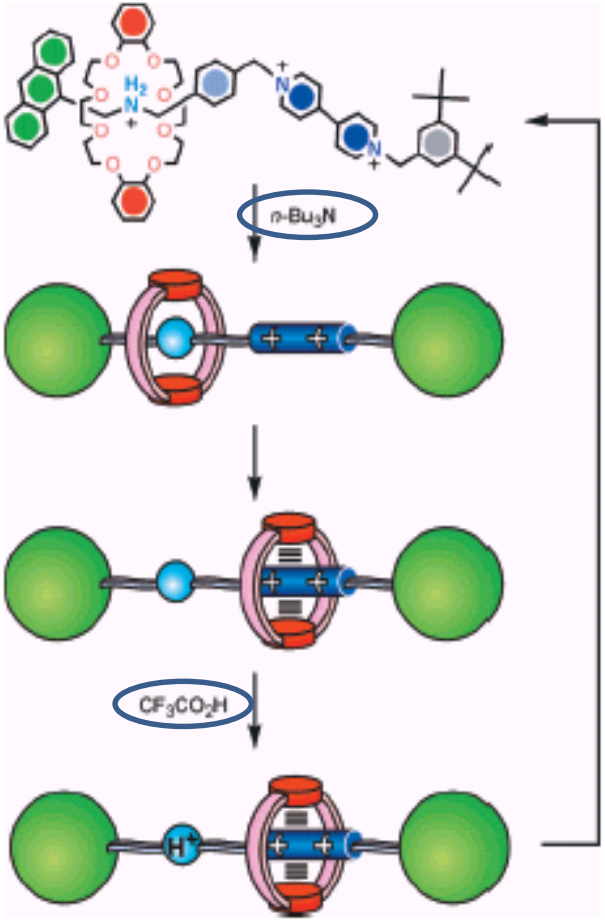
Figure 2. Experimental geometry used[19] to observe single myosin molecules binding and pulling an actin filament. The filament was attached at either end to a trapped bead. These beads were used to stretch the filament taut and move it near surface-bound silica beads that were decorated sparsely with myosin molecules. Adapted with permission from ref. [19] (Copyright© Macmillan Magazines Ltd 1994).

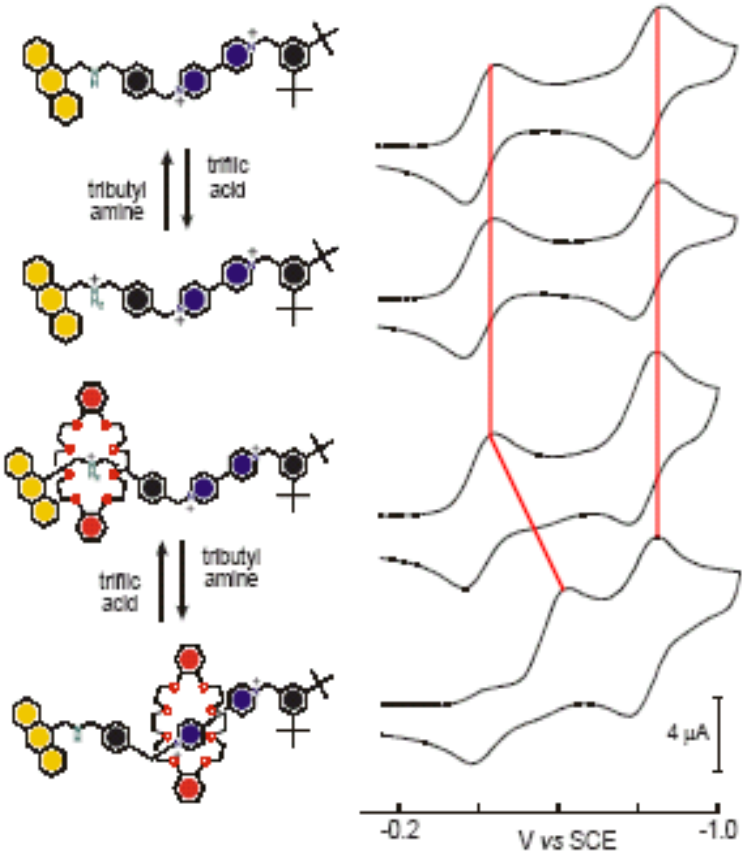

shuttling


ring
rotation

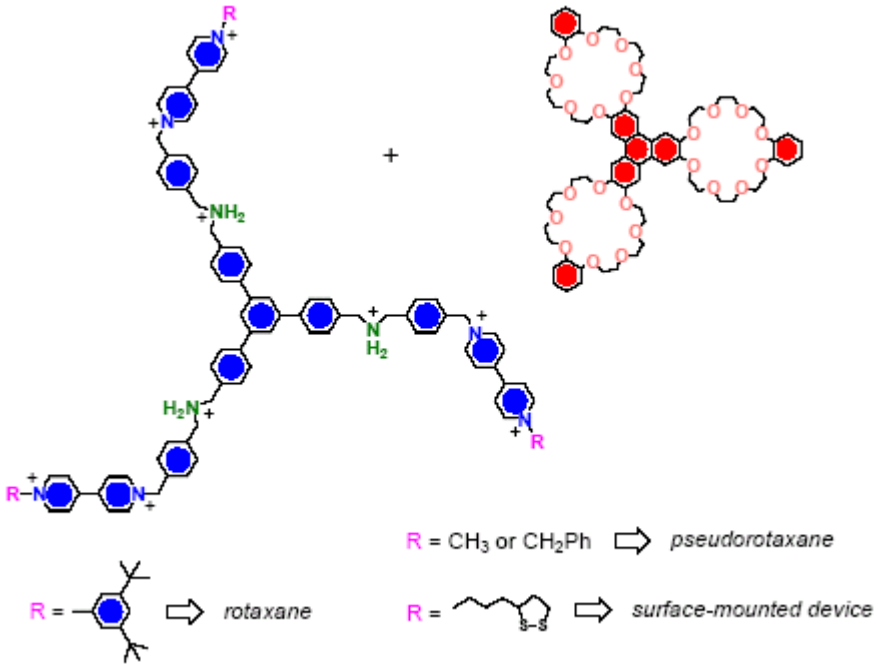

Electron
donor/acceptor
interactions
Hydrogen
bonding
interactions

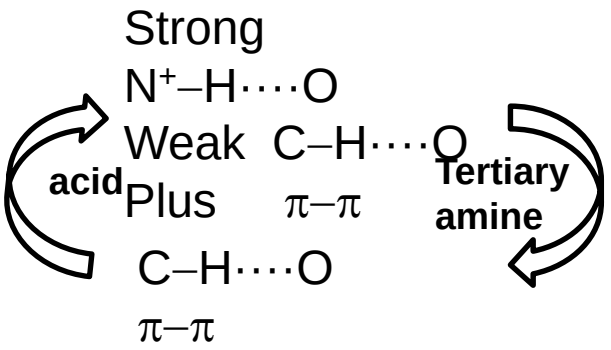
Input chimico

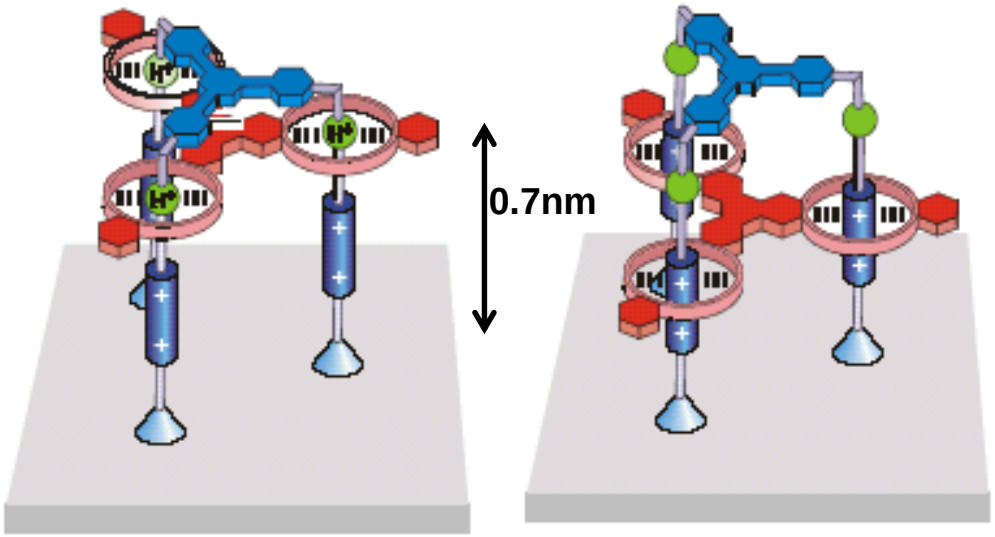


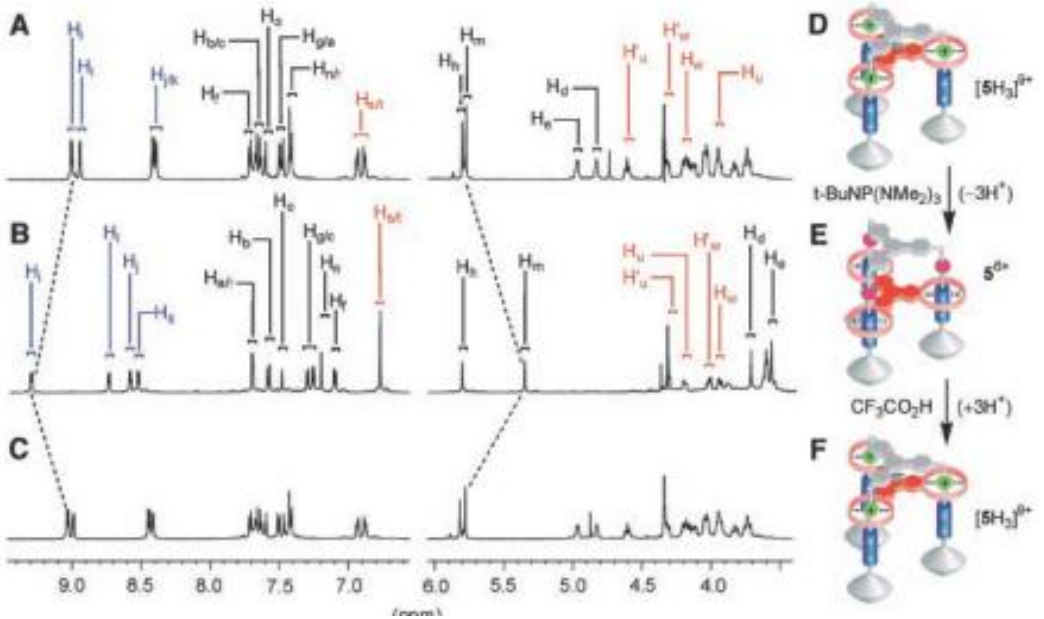


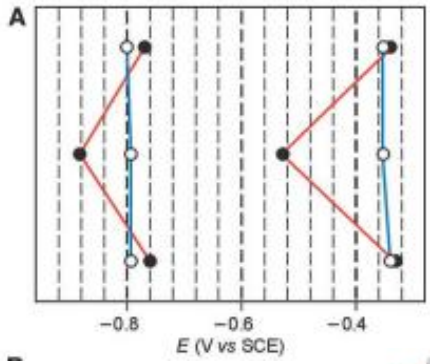
Ascensore molecolare

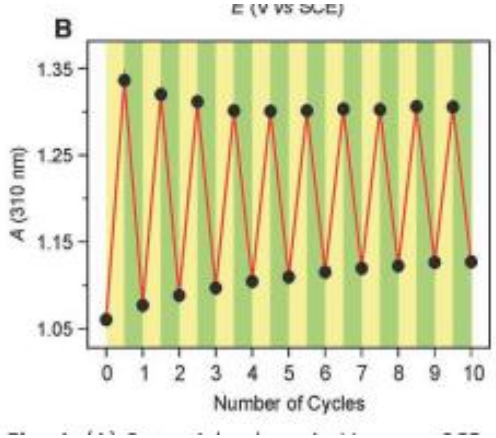


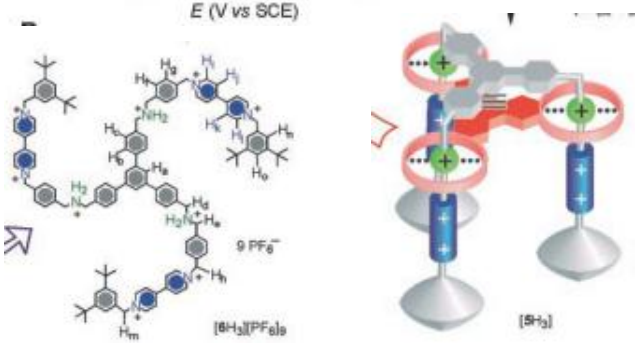


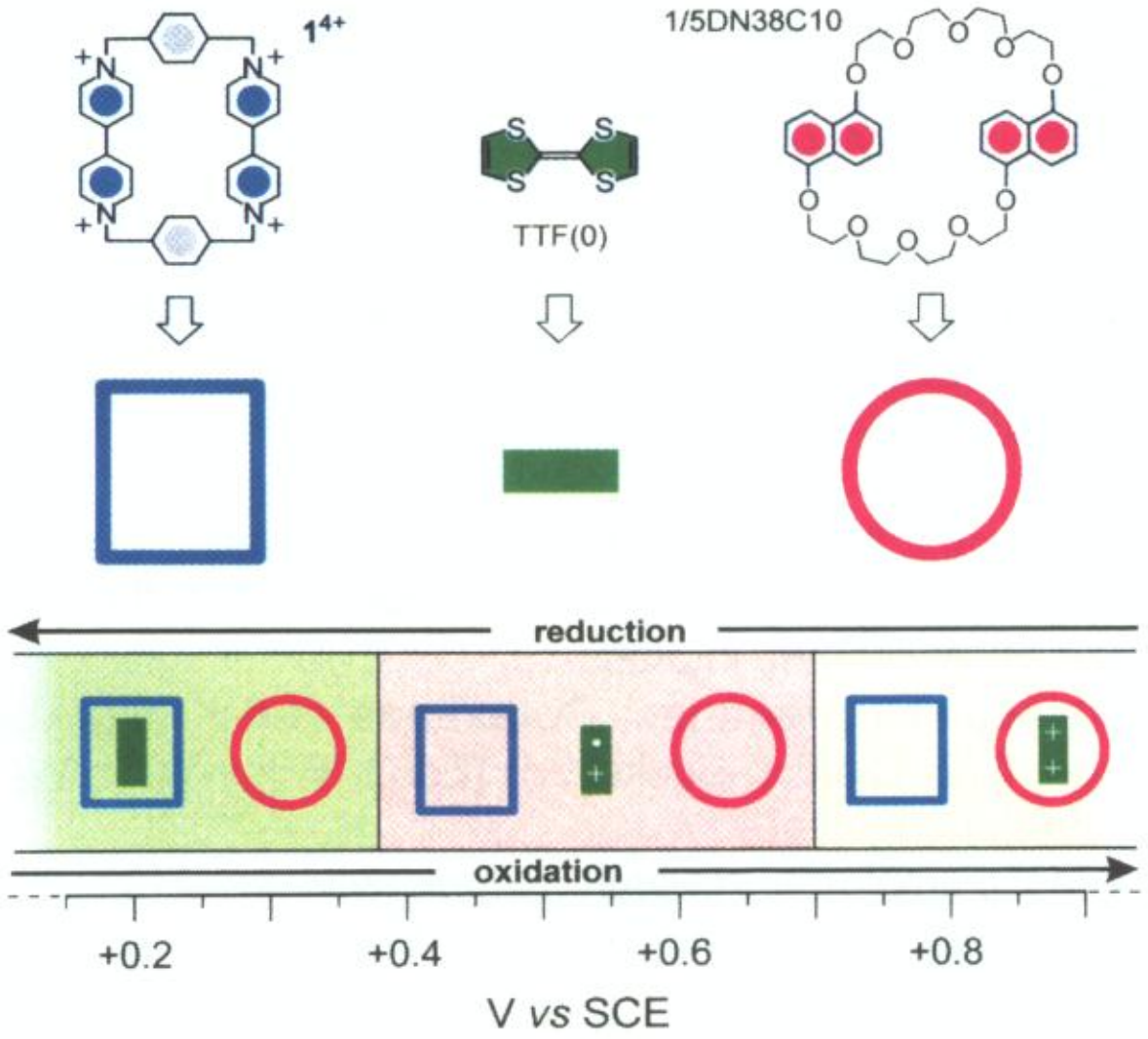



A
B
C
D
E
F
9.0
8.5
8.0
7.5
7.0
6.0
5.5
5.0
4.5
4.0
t-BuNP(NMe2)3 (−3H+)
CF3CO2H (+3H+)
[5H3]9+
5 6+
[5H3]9+

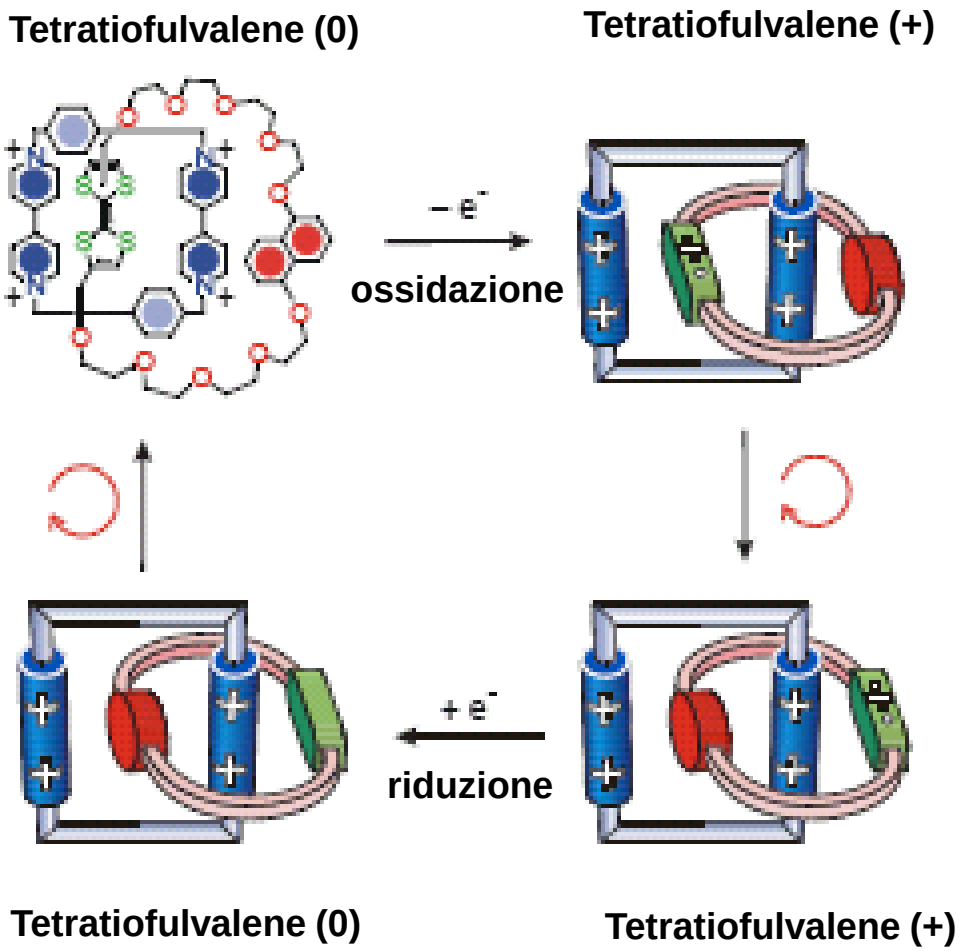

A
−0.8
−0.6
−0.4
E (V vs SCE)


B
A (310 nm)
1.35
1.25
1.15
1.05
0
1
2
3
4
5
6
7
8
9
10
Number of Cycles


9 PF6−
[6H3][PF6]9
[5H3]


1/5DN38C10
TTF(0)
reduction
oxidation
+0.2
+0.4
+0.6
+0.8
V vs SCE

Input elettrochimico



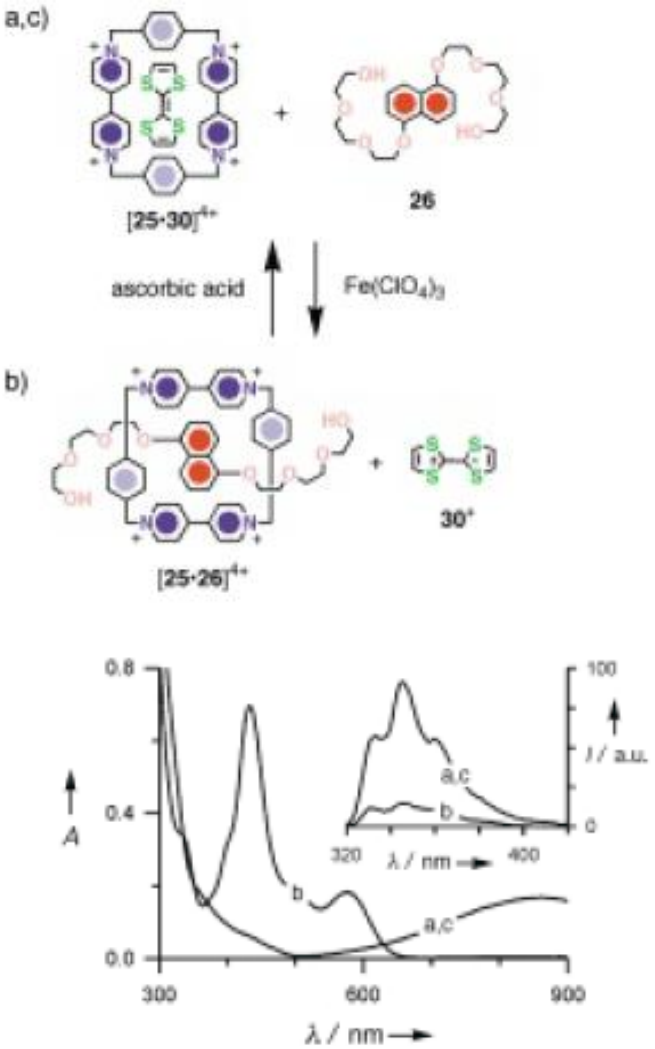
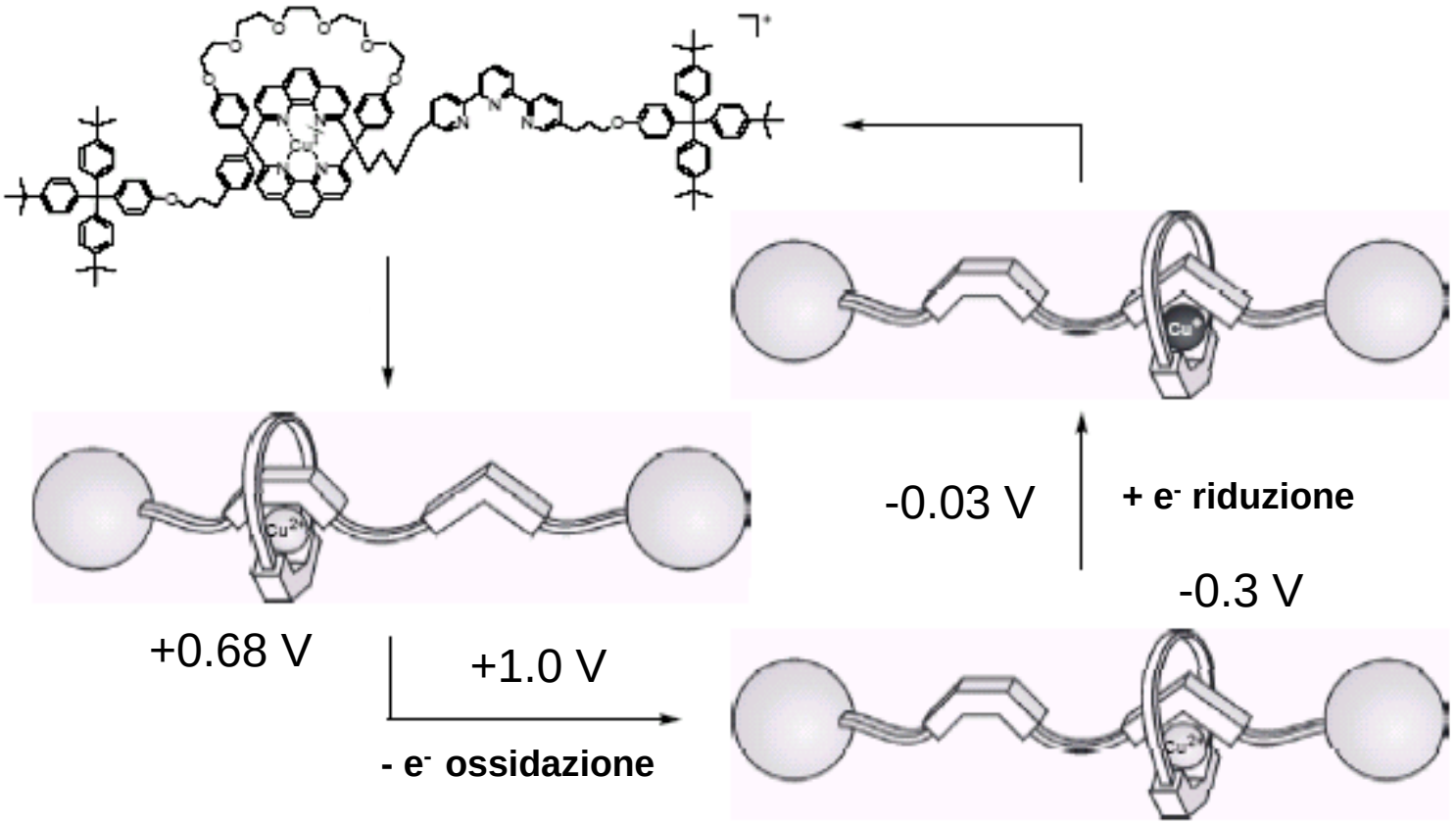


Figure 4. Top: the chemically induced interchange of guests **26** and **30** into the cavity of cyclophane $\mathbf{25}^{4+}$.[93] Bottom: absorption and (inset) fluorescence ($\lambda_{exc} = 295$ nm) spectra of a) a 5×10^{-5} M aqueous solution (298 K) of $[\mathbf{25 \cdot 30}]^{4+}$ and **26;** b) the same solution after addition of one equivalent of $Fe(ClO_4)_3$; c) solution b) after addition of one equivalent of ascorbic acid.

Input elettrochimico



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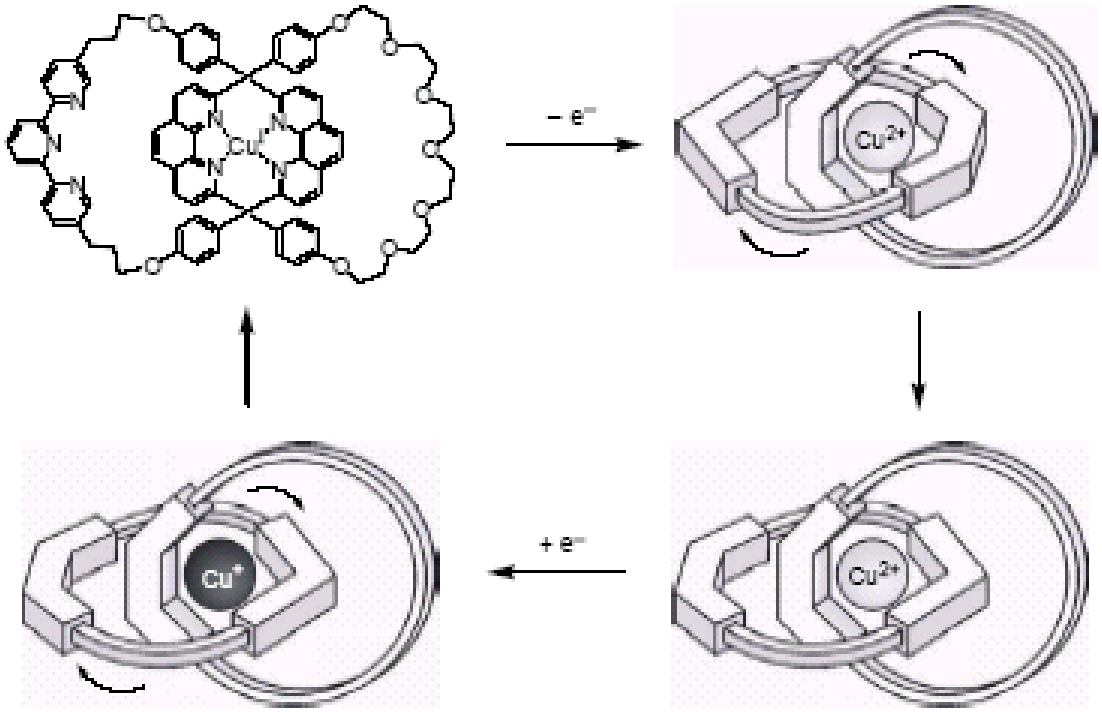
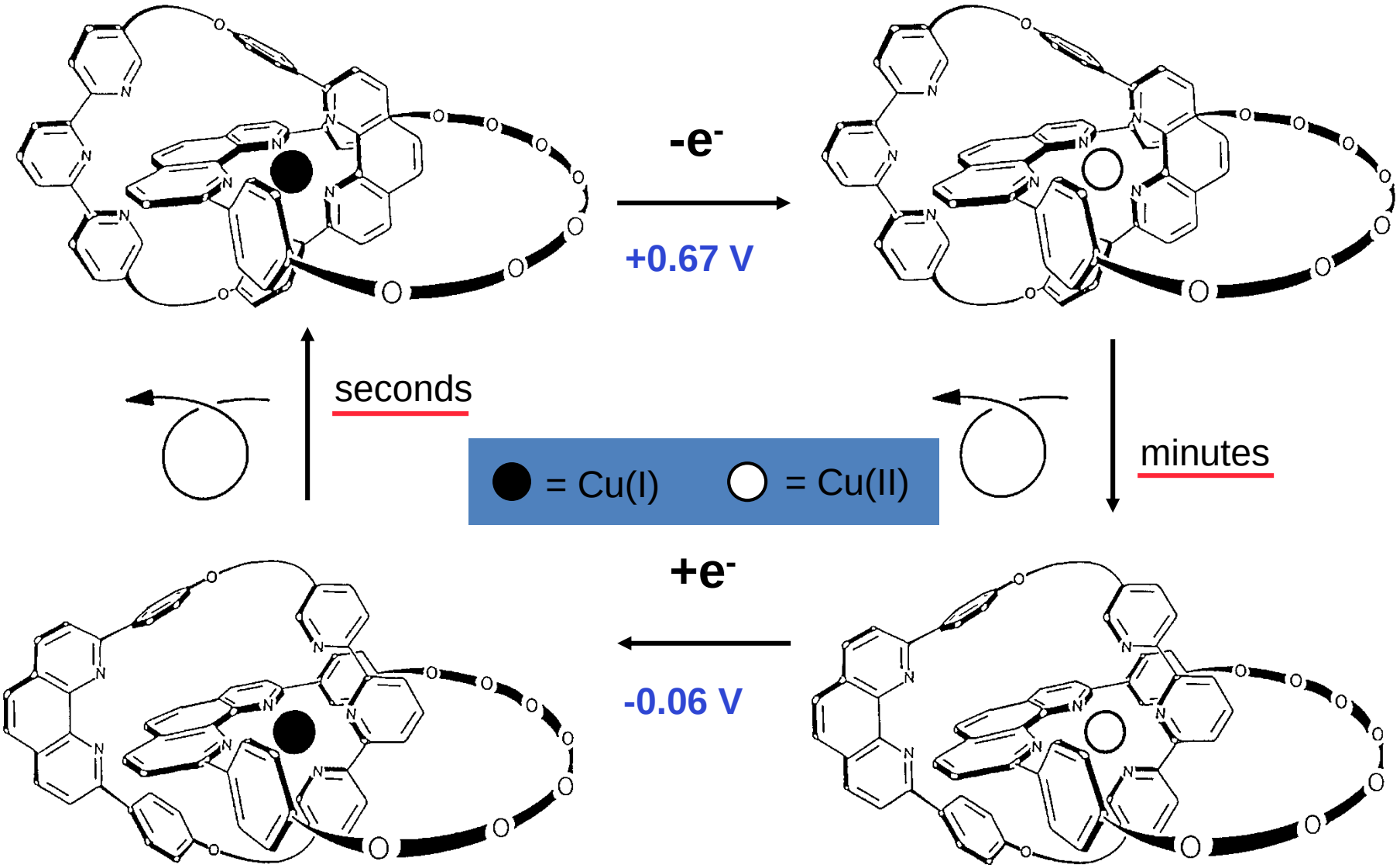
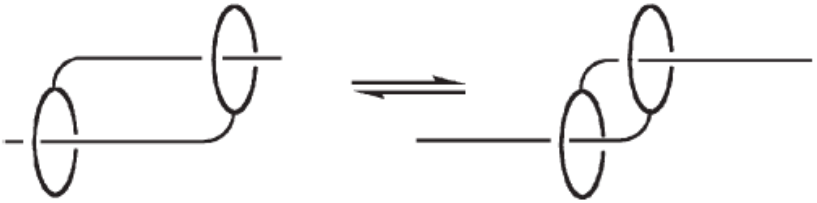
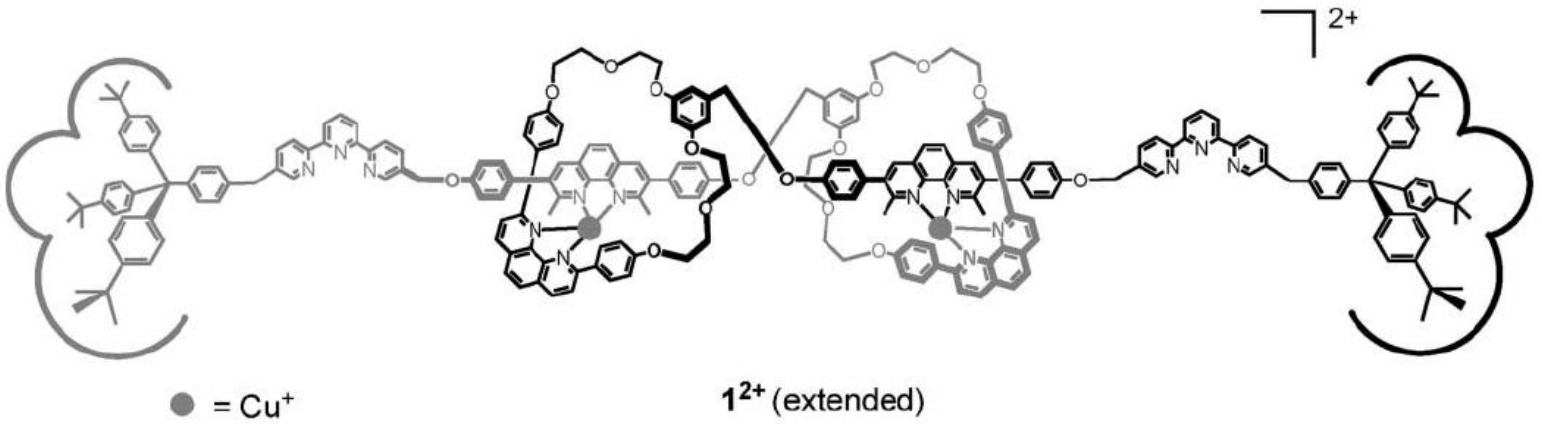



-e-
+0.67 V
seconds
minutes
= Cu(I)
= Cu(II)
+e-
-0.06 V

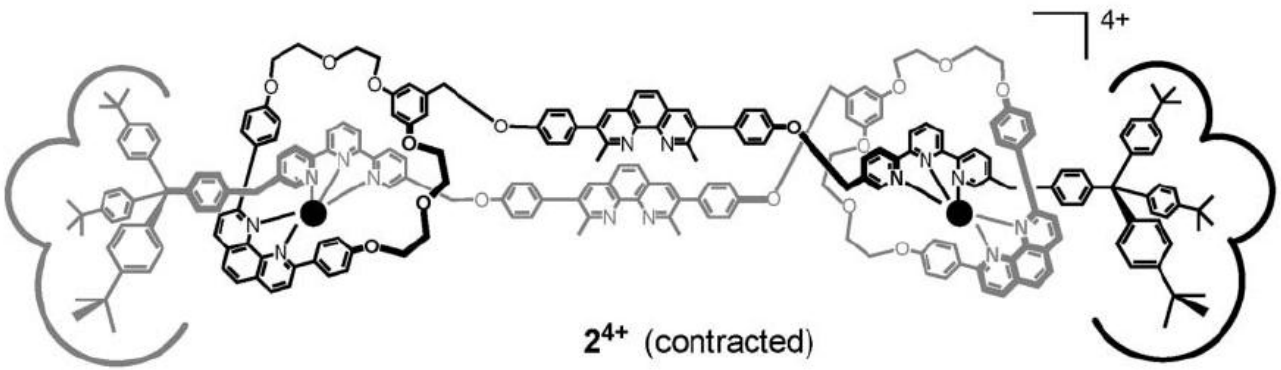
Input chimico





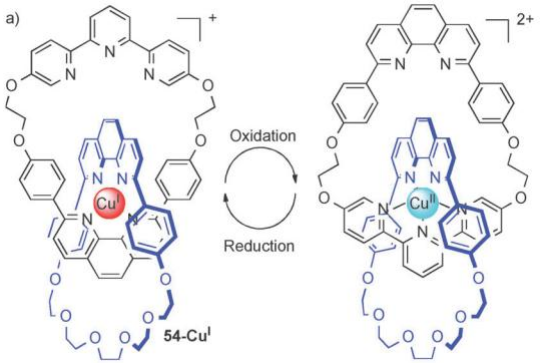
● = Cu^{+}

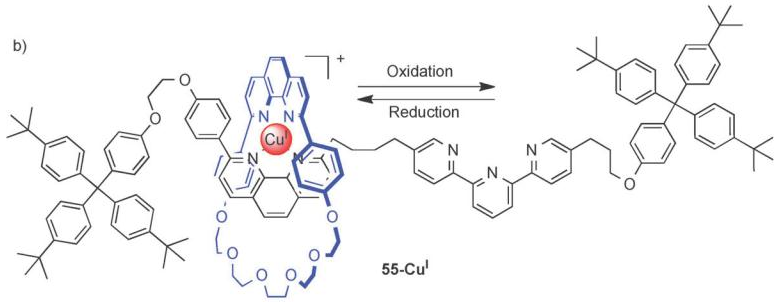
1^{2+} (extended)

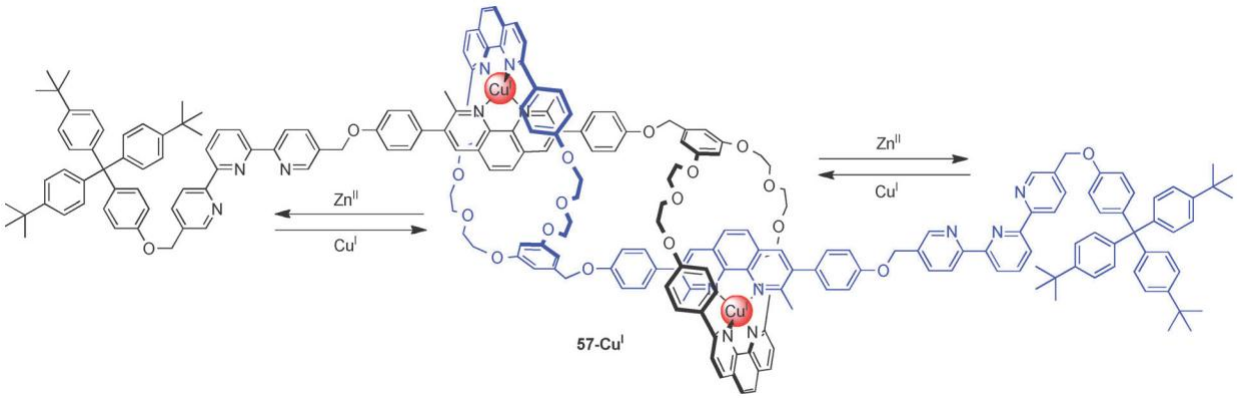


2^{4+} (contracted)

● = Zn^{2+}


a)
Oxidation
Reduction
54-Cu^{I}


b)
Oxidation
Reduction
55-Cu^{I}


Zn^{II}
Cu^{I}
Zn^{II}
Cu^{I}
57-Cu^{I}

Input fotochimico

Unidirectional rotation in a mechanically interlocked molecular rotor

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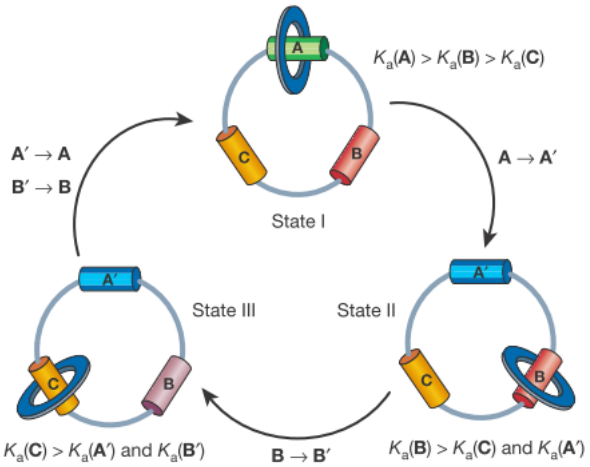
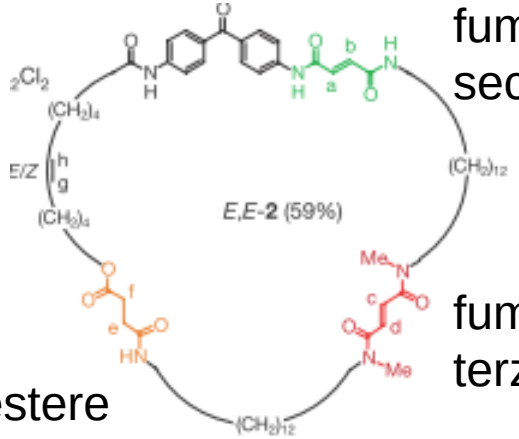
** School of Chemistry, University of Edinburgh, The King's Buildings, West Mains Road, Edinburgh EH9 3JJ, UK*
† Dipartimento di Chimica 'G. Ciamician', Universita degli Studi di Bologna, via F. Selmi 2, 40126 Bologna, Italy



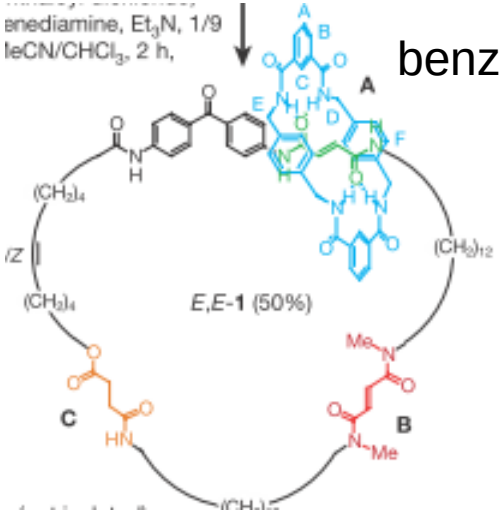
benzofenone



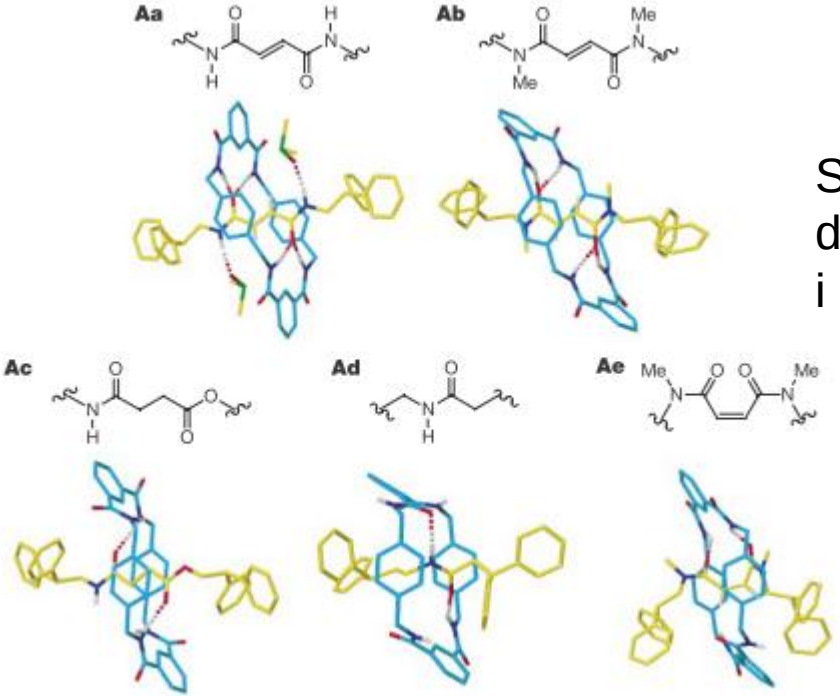
fumaramide secondaria *E*

fumaramide terziaria *E*

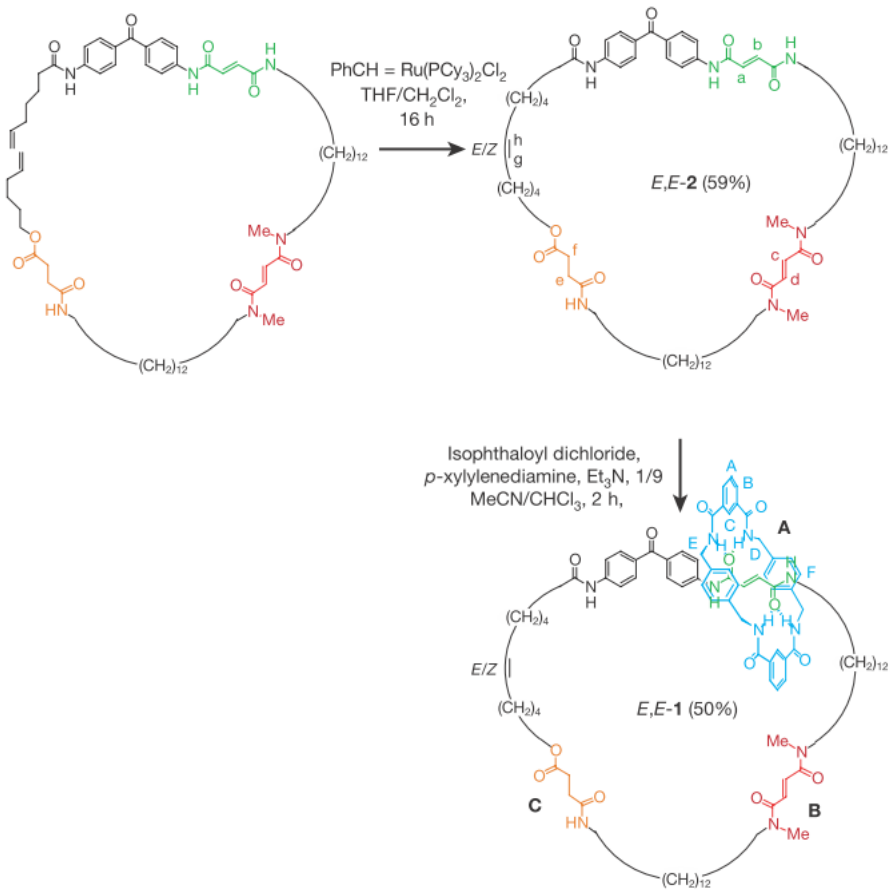
estere succinamidico

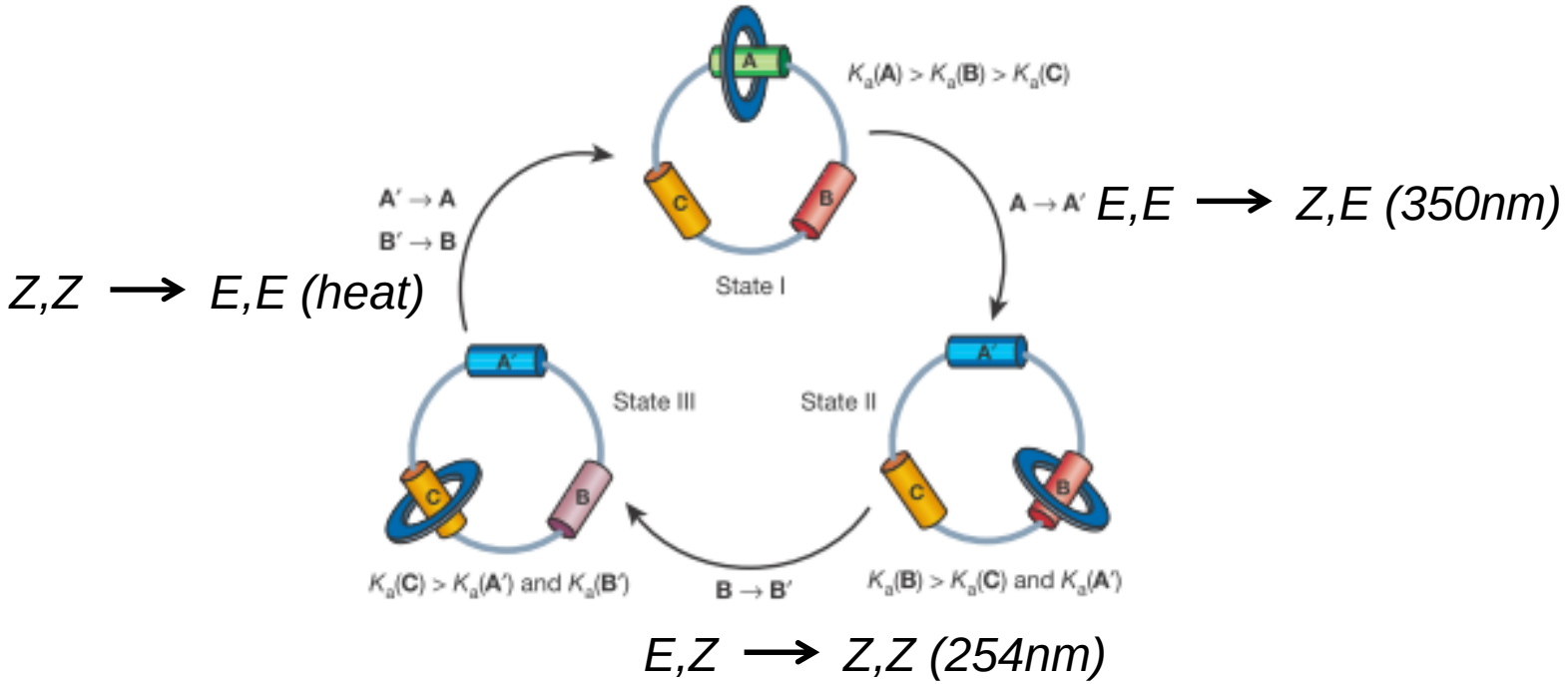


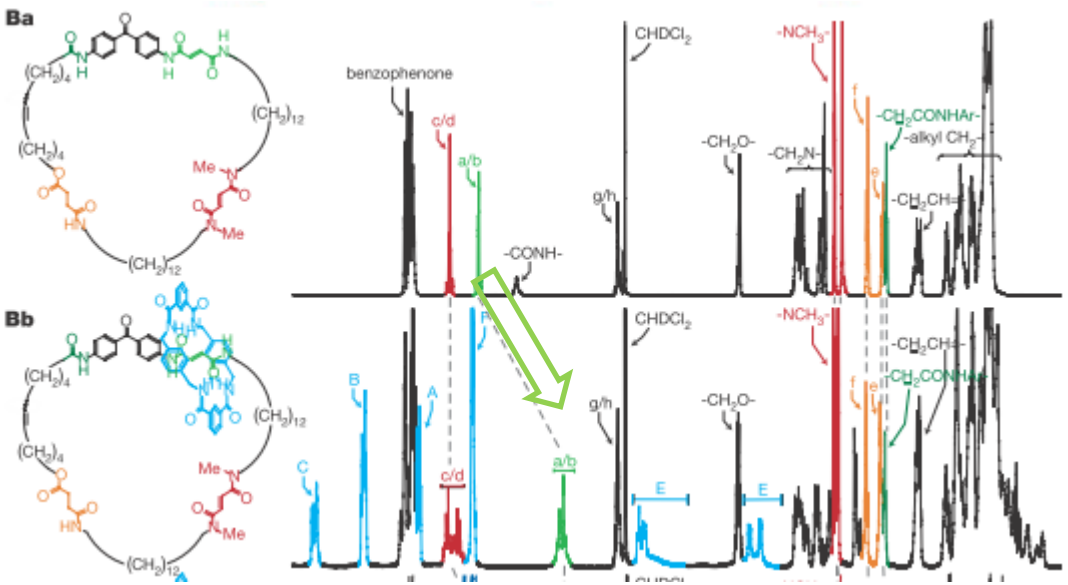
benzilamide

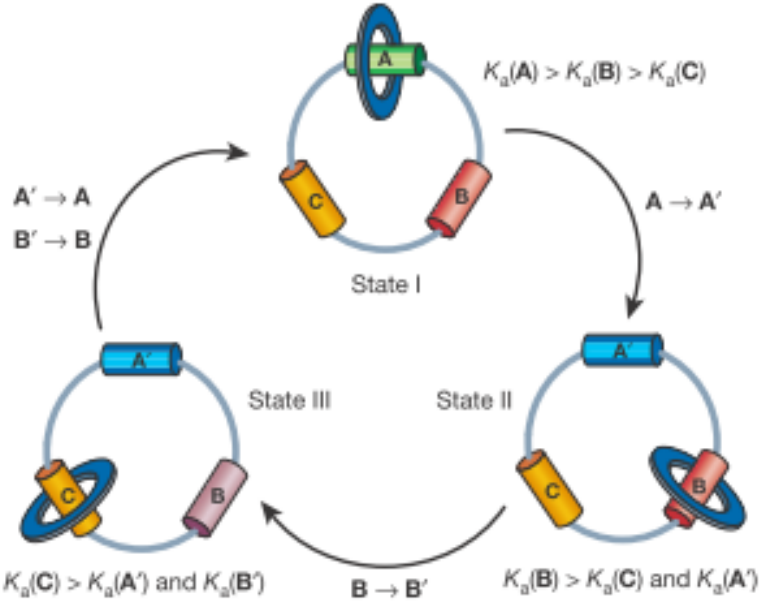


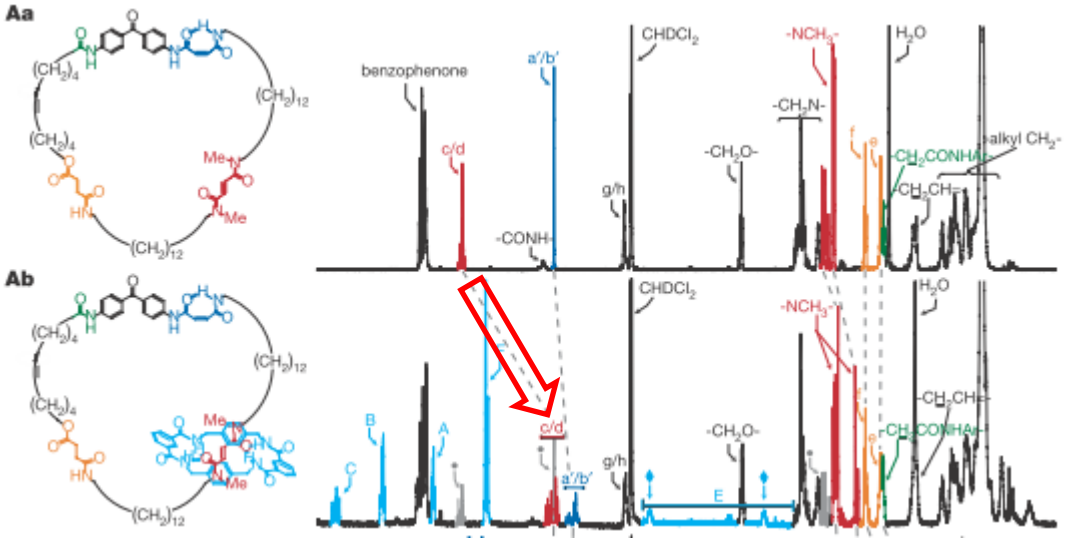
Strutture ai raggi X dei siti di binding dei modelli [2] rotaxani con indicati i legami idrogeno (in ordine di affnità)

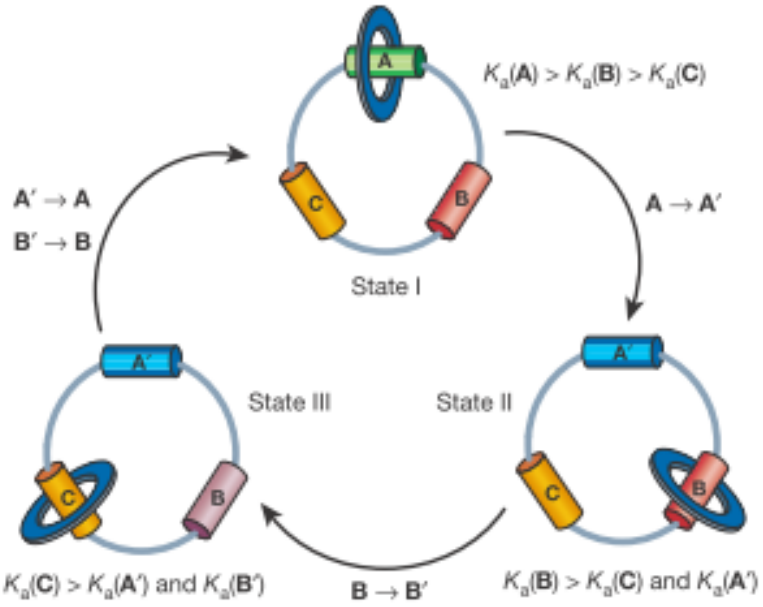

PhCH = Ru(PCy3)2Cl2
THF/CH2Cl2,
16 h
E/Z
E,E-2 (59%)
Isophthaloyl dichloride,
p-xylylenediamine, Et3N, 1/9
MeCN/CHCl3, 2 h,
E/Z
E,E-1 (50%)
A
B
C
(CH2)12
(CH2)4
Me
HN

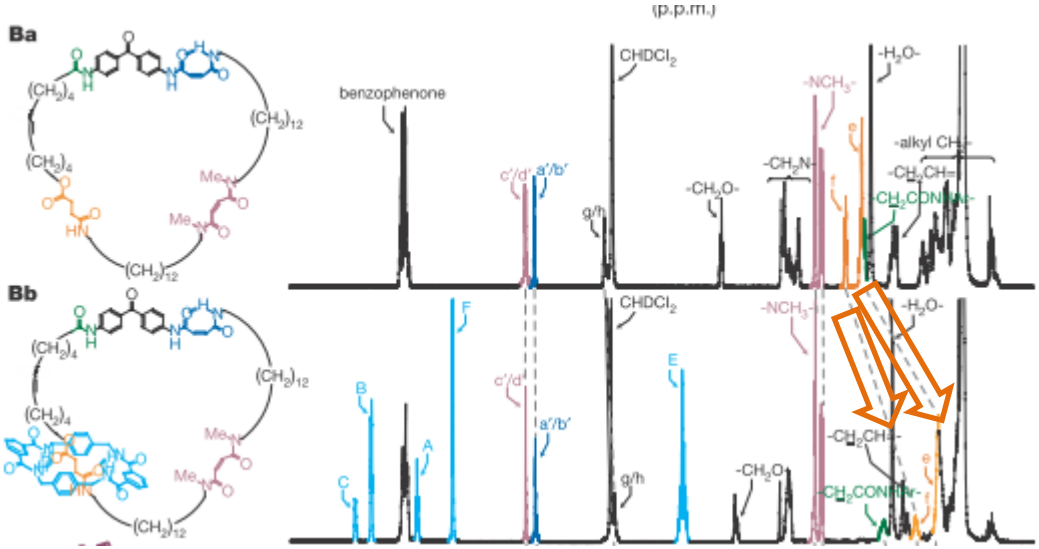

Z,Z ⟶ E,E (heat)
A′ → A
B′ → B
K_a(A) > K_a(B) > K_a(C)
A → A′ E,E ⟶ Z,E (350nm)
State I
State II
State III
K_a(C) > K_a(A′) and K_a(B′)
B → B′
K_a(B) > K_a(C) and K_a(A′)
E,Z ⟶ Z,Z (254nm)

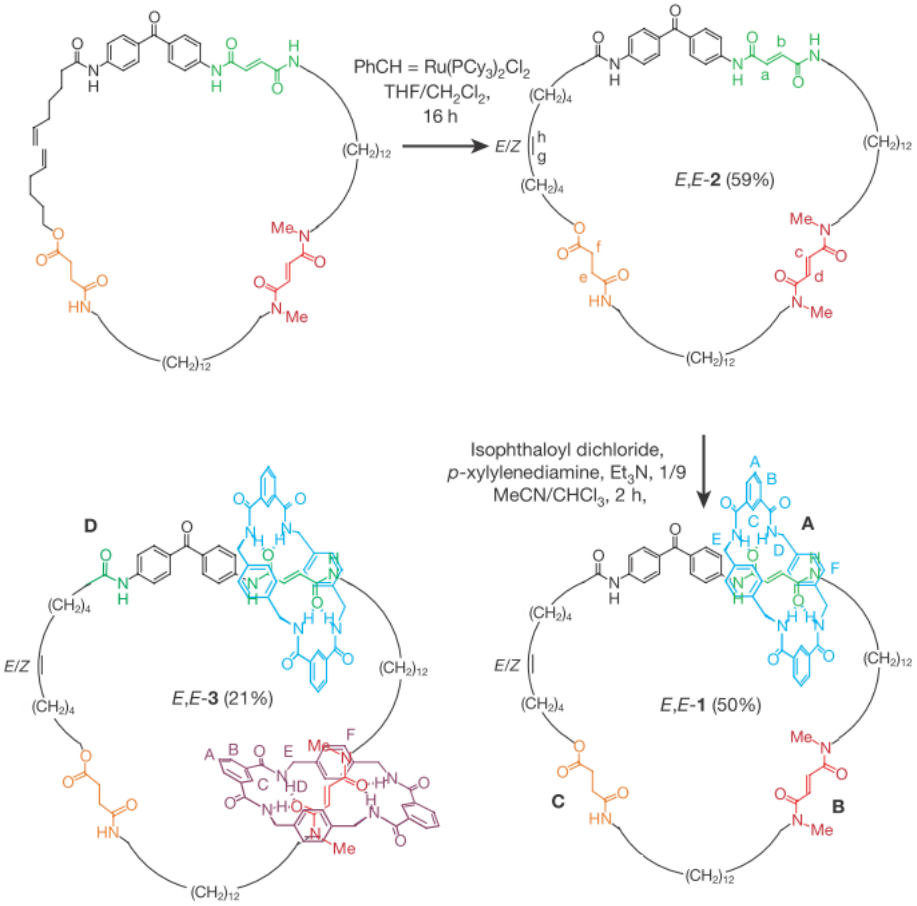

Ba
Bb
benzophenone
CHDCl2
-NCH3-
-CH2O-
-CH2N-
-CH2CONHAr-
-alkyl CH2-
-CH2CH=
-CONH-
g/h
c/d
a/b
A
B
C
E
Me
HN
(CH2)4
(CH2)12

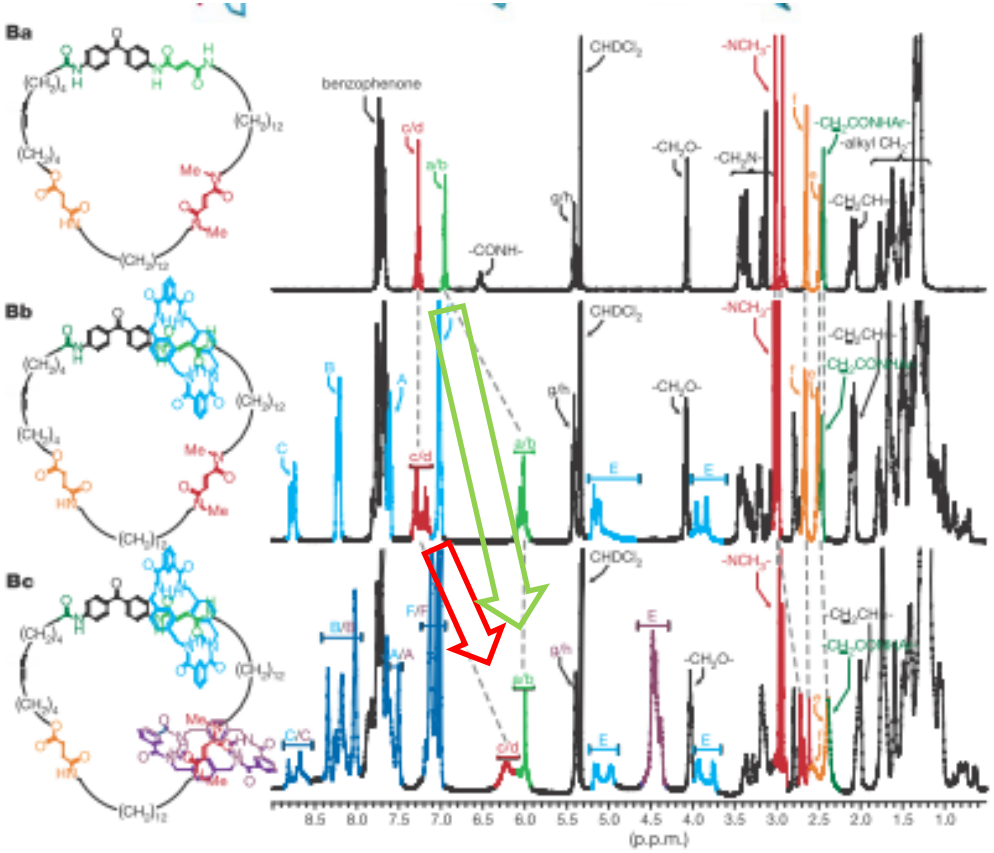

A
B
C
K_a(A) > K_a(B) > K_a(C)
A → A′
State I
State II
A′
B
C
K_a(B) > K_a(C) and K_a(A′)
B → B′
State III
A′
B
C
K_a(C) > K_a(A′) and K_a(B′)
A′ → A
B′ → B


Aa
Ab
benzophenone
a′/b′
CHDCl2
-NCH3-
H2O
-CH2N-
c/d
-CH2O-
g/h
-CONH-
-CH2CONHAr-
-alkyl CH2-
-CH2CH2-
A
B
C
E
Me
N
O
HN
(CH2)4
(CH2)12


A
B
C
State I
$K_a(\mathbf{A}) > K_a(\mathbf{B}) > K_a(\mathbf{C})$
$\mathbf{A} \rightarrow \mathbf{A}'$
State II
A′
B
C
$K_a(\mathbf{B}) > K_a(\mathbf{C})$ and $K_a(\mathbf{A}')$
$\mathbf{B} \rightarrow \mathbf{B}'$
State III
A′
B
C
$K_a(\mathbf{C}) > K_a(\mathbf{A}')$ and $K_a(\mathbf{B}')$
$\mathbf{A}' \rightarrow \mathbf{A}$
$\mathbf{B}' \rightarrow \mathbf{B}$

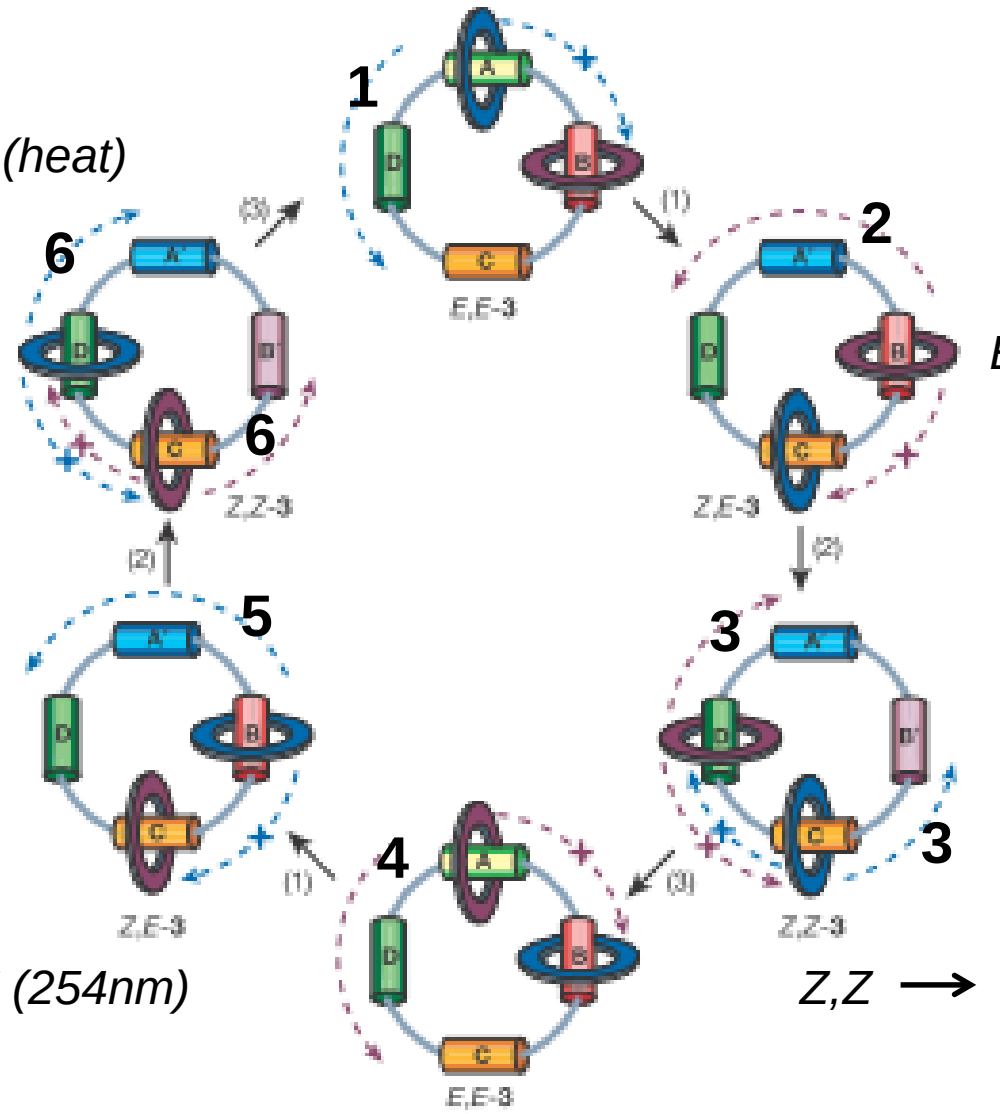

Ba
Bb
(p.p.m.)
benzophenone
CHDCl2
-NCH3-
-H2O-
-CH2O-
-CH2N-
-alkyl CH2-
-CH2CH=
-CH2CONHN-
c′/d′
a′/b′
g/h
e
f
F
E
B
A
C
-CH2CH-


PhCH = Ru(PCy3)2Cl2
THF/CH2Cl2,
16 h
E/Z
E,E-2 (59%)
Isophthaloyl dichloride,
p-xylylenediamine, Et3N, 1/9
MeCN/CHCl3, 2 h,
E,E-3 (21%)
E,E-1 (50%)
A
B
C
D


Ba
Bb
Bc
benzophenone
c/d
a/b
-CONH-
g/h
CHDCl2
-CH2O-
-CH2N-
-NCH3-
-CH2CONHAr-
-alkyl CH2-
-CH2CH-
B
A
C
E
F/F'
A/A'
B/B'
C/C'
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0
(p.p.m.)

E,E ⟶ Z,E (350nm)

Z,Z ⟶ E,E (heat)



E,Z ⟶ Z,Z (254nm)

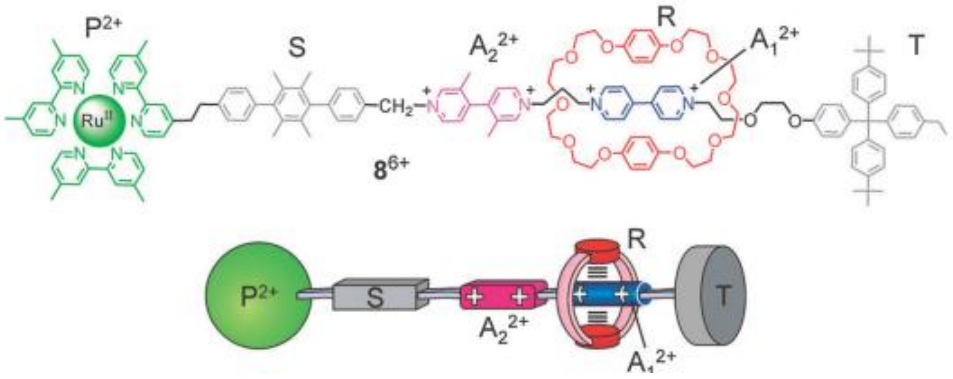
E,Z ⟶ Z,Z (254nm)

Z,Z ⟶ E,E (heat)

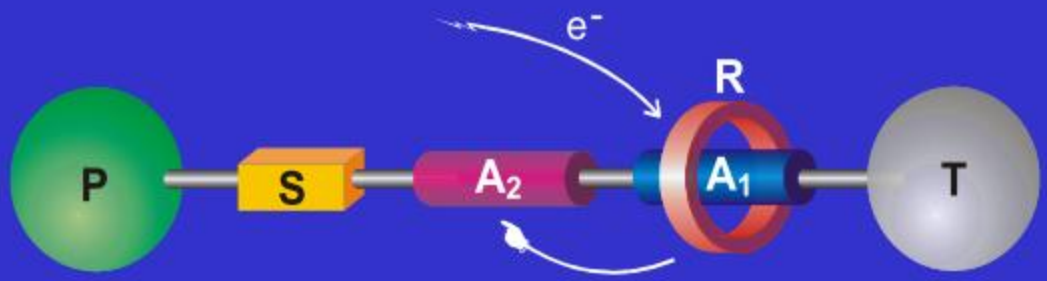
E,E ⟶ Z,E (350nm)

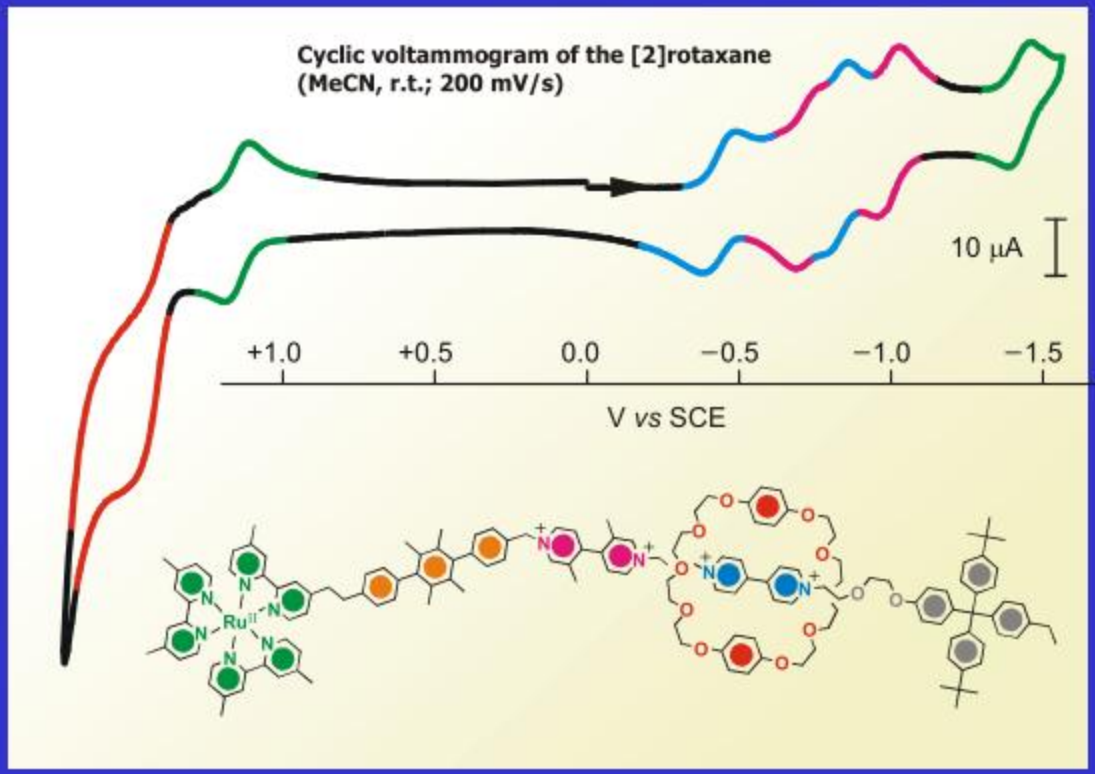
Input fotochimico

Ru(II)polypyridine complex (P^{2+})
p-terphenyl-type rigid spacer (S)
4,4'-bipyridinium (A_1^{2+})
3,3'-dimethyl-4,4'-bipyridinium (A_2^{2+})
Tetraarylmethane group (T)
Six PF_6^- counterions



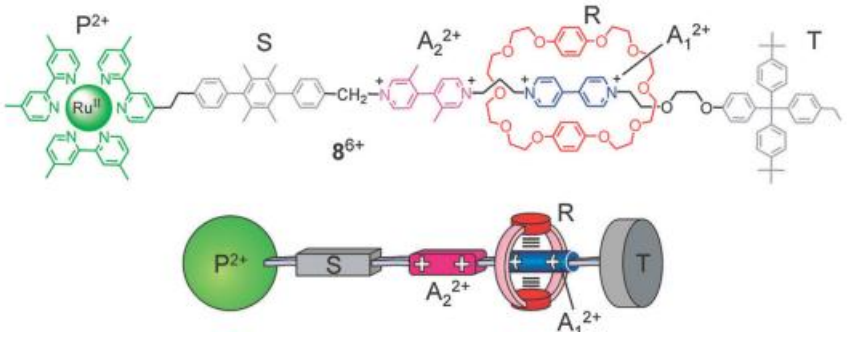
a) Redox-induced ring motion

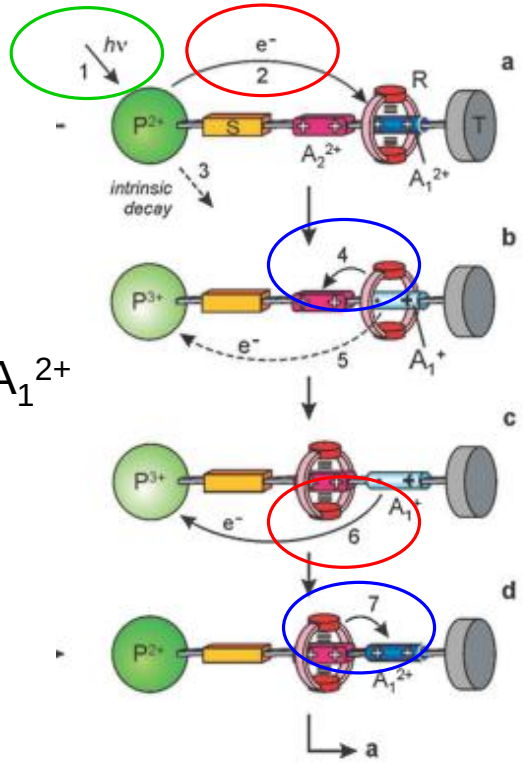




Input fotochimico

Ru(II)polypyridine complex (P^{2+})
p-terphenyl-type rigid spacer (S)
4,4'-bipyridinium (A_1^{2+})
3,3'-dimethyl-4,4'-bipyridinium (A_2^{2+})
Tetraarylmethane group (T)
Six PF_6^- counterions





1 $P^{2+} \longrightarrow {}^*P^{2+}$

2 ${}^*P^{2+} + A_1^{2+} \longrightarrow P^{3+} + A_1^{1+}$
-0.8 V -0.44 V

3 ${}^*P^{2+} \longrightarrow P^{2+}$

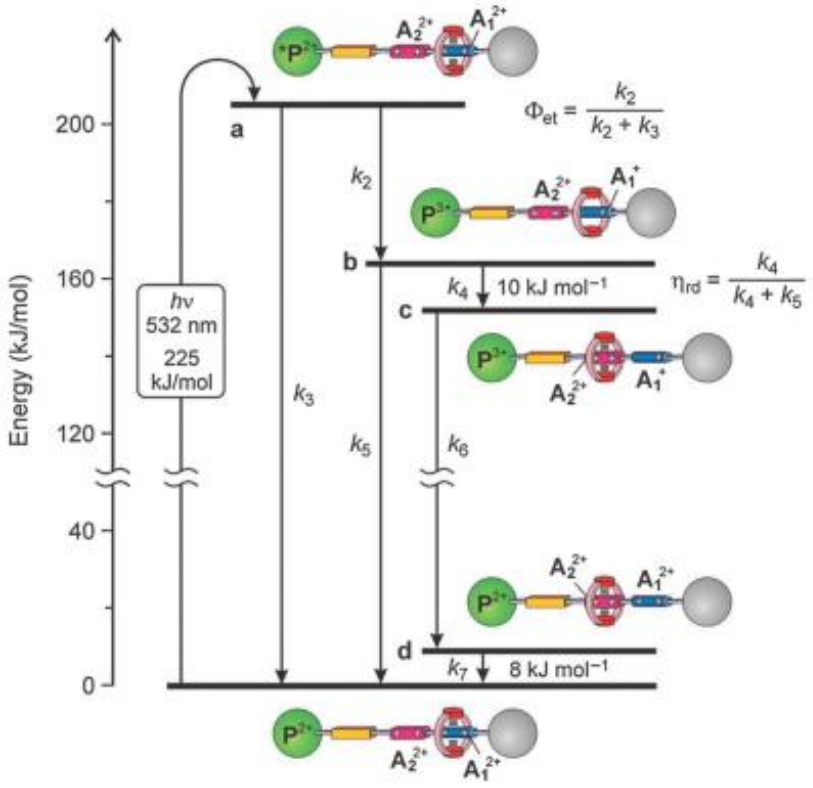
4 Shuttling (5 nm)

5 $P^{3+} + A_1^{1+} \longrightarrow {}^*P^{2+} + A_1^{2+}$

6 $P^{3+} + A_1^{1+} \longrightarrow P^{2+} + A_1^{2+}$

7 Shuttling (5 nm)

Input fotochimico



1 $P^{2+} \longrightarrow {}^*P^{2+}$

2 ${}^*P^{2+} + A_1^{2+} \longrightarrow P^{3+} + A_1^{1+}$

4 Shuttling (5 nm)

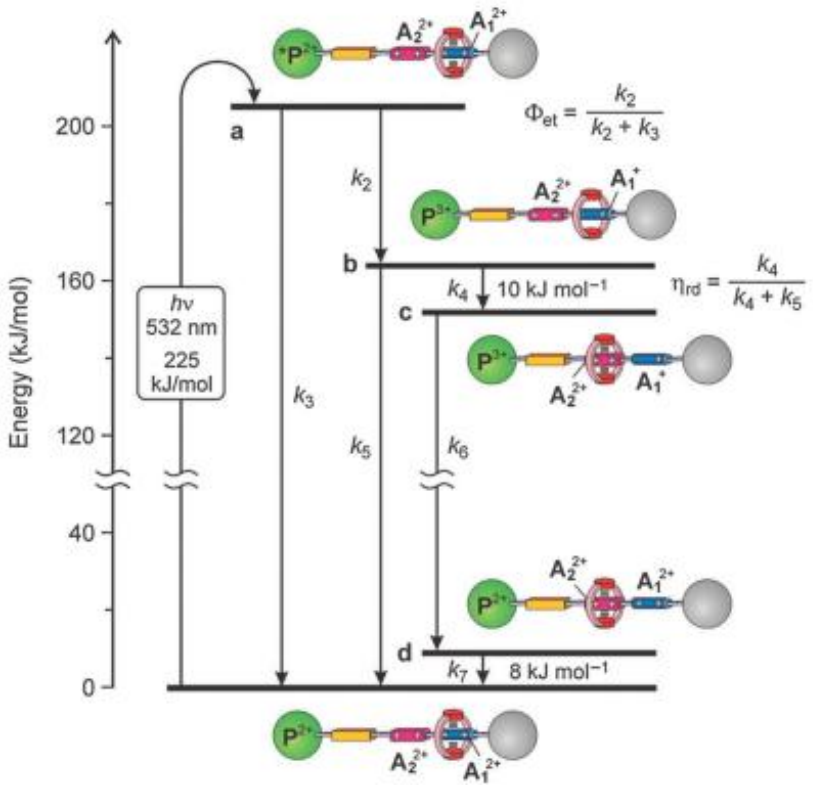
6 $P^{3+} + A_1^{1+} \longrightarrow P^{2+} + A_1^{2+}$

7 Shuttling (5 nm)

3 ${}^*P^{2+} \longrightarrow P^{2+}$

5 $P^{3+} + A_1^{1+} \longrightarrow {}^*P^{2+} + A_1^{2+}$

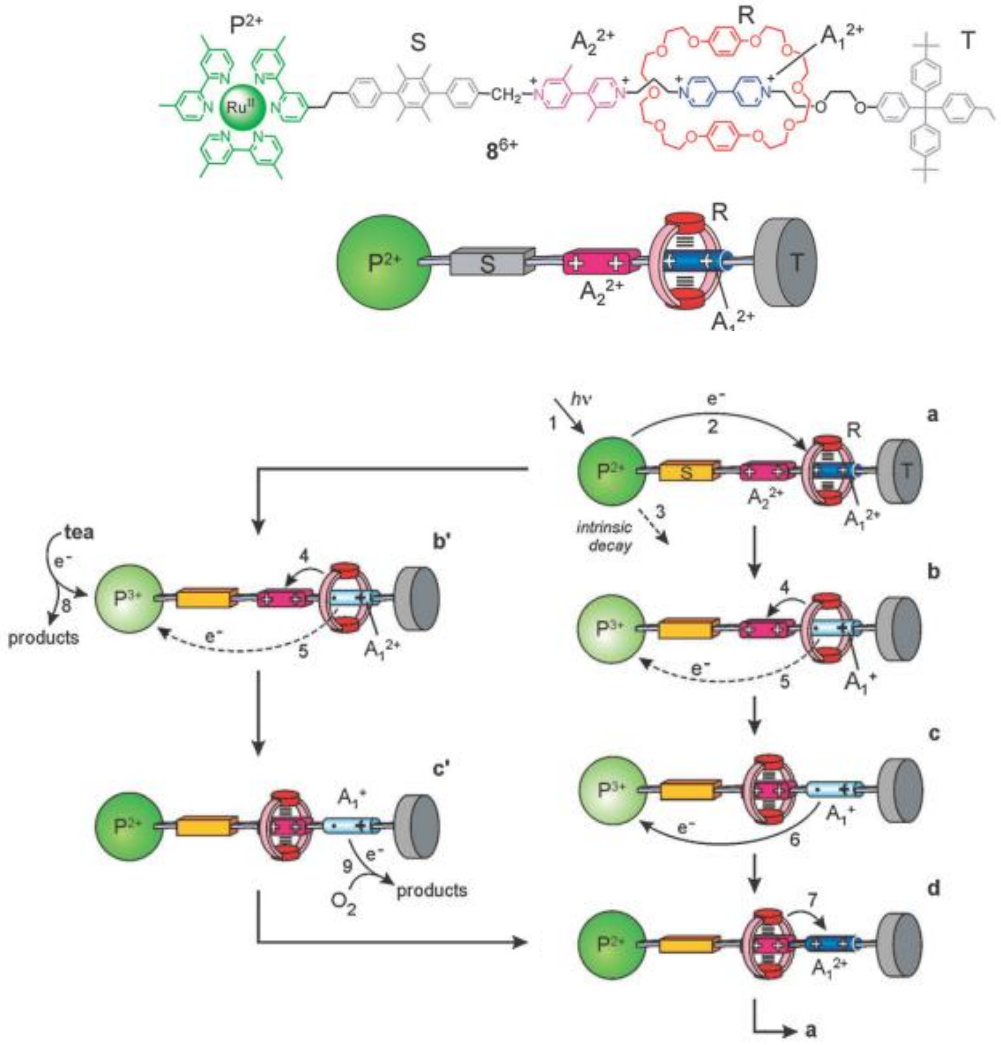
Input fotochimico

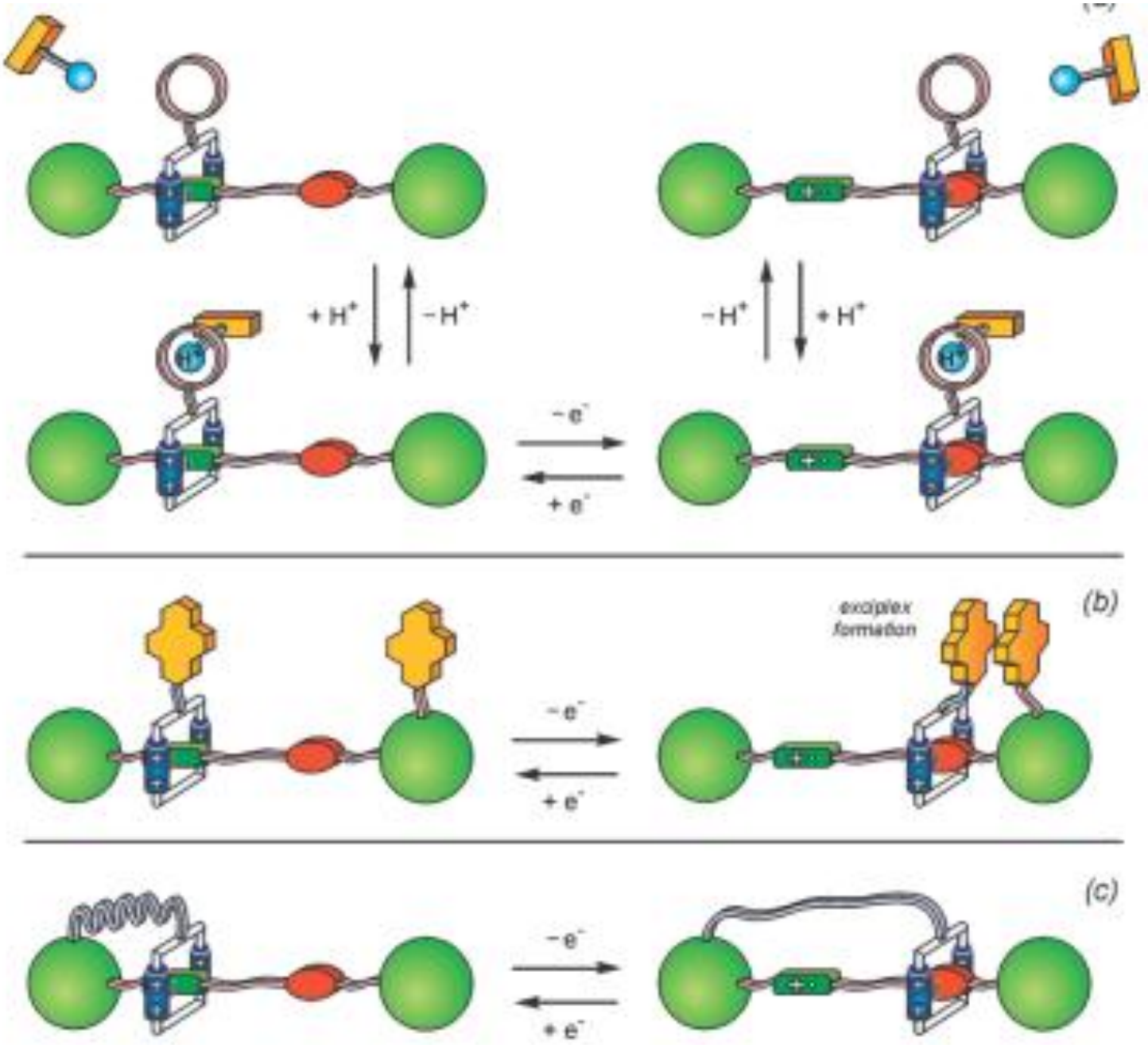


Hence, the fraction F of the excited state energy (205 kJ mol^{-1}) used for the motion of the ring amounts to *ca.* 10%, and the overall efficiency of the machine is $\eta = \Phi_{sh} \times F = 0.2\%$.

This somewhat disappointing result is compensated by the fact that the investigated system gathers together the following features: (i) it is powered by visible light (in other words, sunlight); (ii) it exhibits autonomous behaviour (*i.e.*, like natural molecular motors, it operates automatically in a constant environment as long as the energy source is available); (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 about 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.

Input fotochimico e chimico (agenti sacrificali TEA e O_2)




+ H+
− H+
− H+
+ H+
− e−
+ e−
(b)
exciplex
formation
− e−
+ e−
(c)
− e−
+ e−