From Chemical Topology to Molecular Machines

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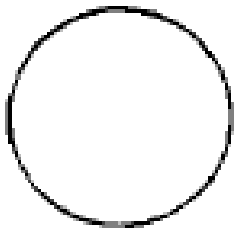
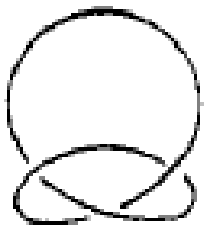
Historical publication : H.L. Frisch & E. Wasserman,
"**Chemical Topology**", *J. Am. Chem. Soc.*, **1961**

Topological isomers :

Planar graph

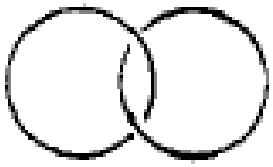


I

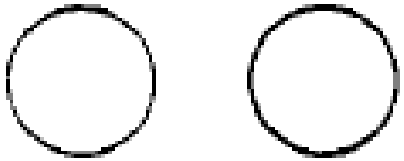


II

Non planar graph



III



IV

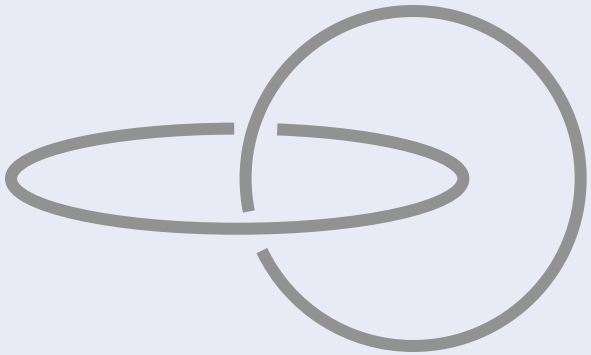
ORGANIC AND BIOLOGICAL CHEMISTRY

[CONTRIBUTION FROM THE BELL TELEPHONE LABORATORIES, INCORPORATED, MURRAY HILL, NEW JERSEY]

Chemical Topology[1]

BY H. L. FRISCH AND E. WASSERMAN

RECEIVED FEBRUARY 28, 1961

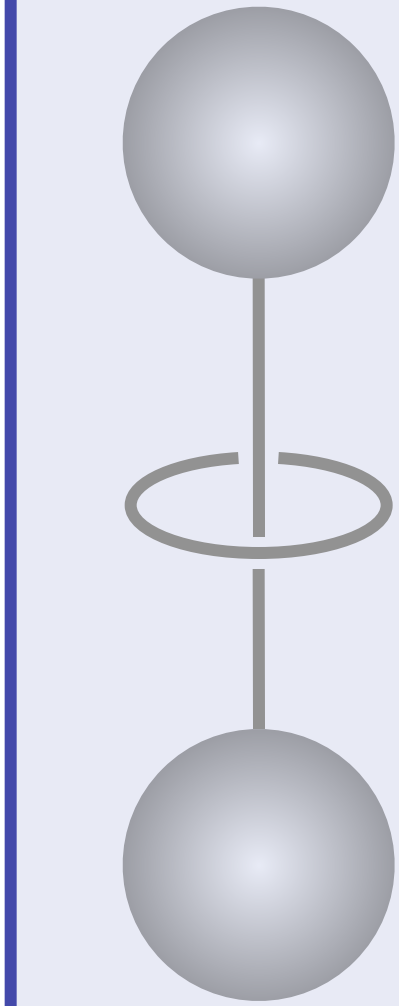


a [2]catenane

The archetype of topologically non trivial compound

Schill & Lüttringhaus could prepare small amounts of such compounds *via* an elegant multistep synthetic route (*Angew. Chem.*, 1964)

Prof. G. Schill - 1984

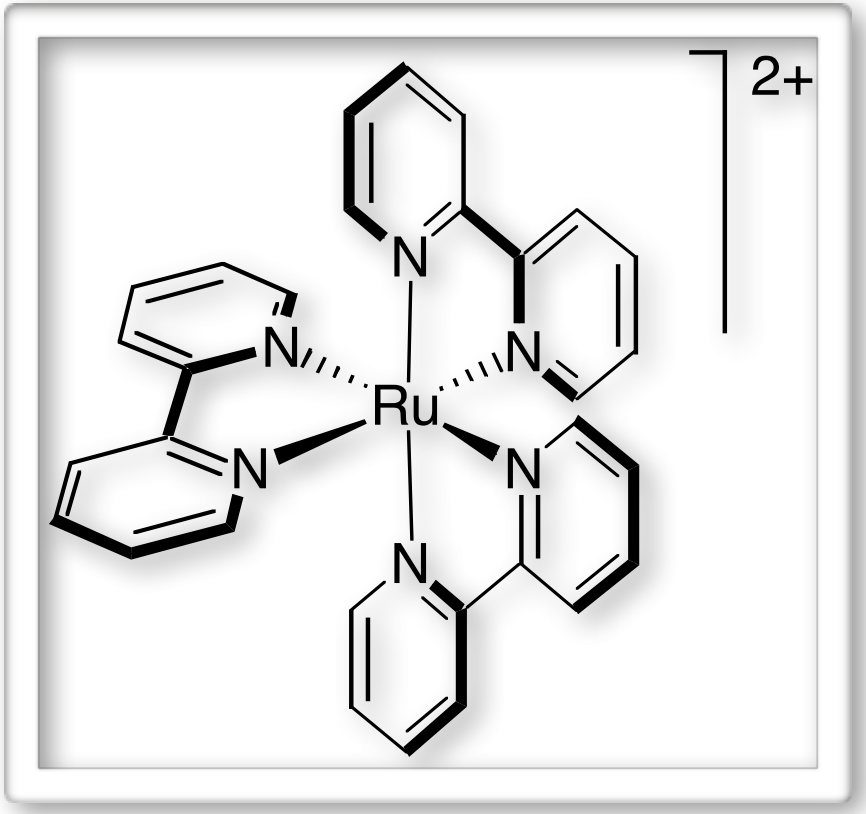


a [2]rotaxane

The long travel from «Inorganic Photochemistry» to Catenanes, Molecular Topology and Molecular Machines

A **grand** project :
Photochemical Cleavage of Water to H_2 and O_2

A very important photoactive transition metal complex : $Ru(bipy)_3^{2+}$



The excited state is able to transfer an electron, a positive charge or electronic energy to a «quencher»

From **ruthenium** to **copper**

Photochemistry of copper(I) complexes with phenanthroline-type ligands

(with the team of D.R. McMillin)

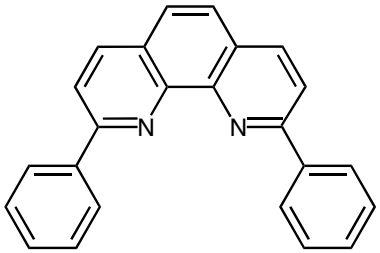
The « story » behind the discovery

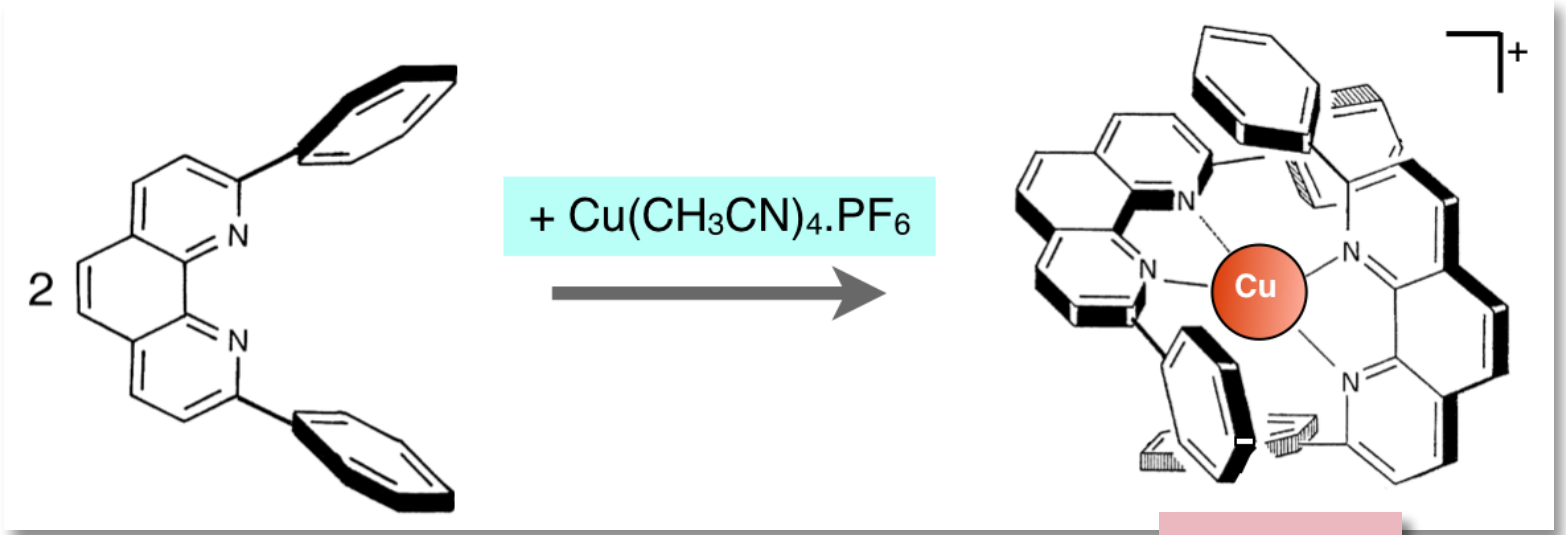
Photochemistry and Photophysics of Copper (I) complexes : *Chem. Comm*. **1983 -** Christiane O. Dietrich-Buchecker, Pascal A. Marnot, Jon R. Kirchhoff and David R. McMillin

David R. McMillin
Purdue University

A sterically hindering ligand :

dpp = 2,9-diphenyl-1,10-phenanthroline





$Cu(dpp)_2^+$

copper(I)-templated synthesis of catenanes and knots

Christiane Dietrich-Buchecker (1942-2008)

The first practical synthesis of catenanes

Tetrahedron Letters,Vol.24,No.46,pp 5095-5098,1983 0040-4039/83 $3.00 + .00
Printed in Great Britain

UNE NOUVELLE FAMILLE DE MOLECULES : LES METALLO-CATENANES

* * * *

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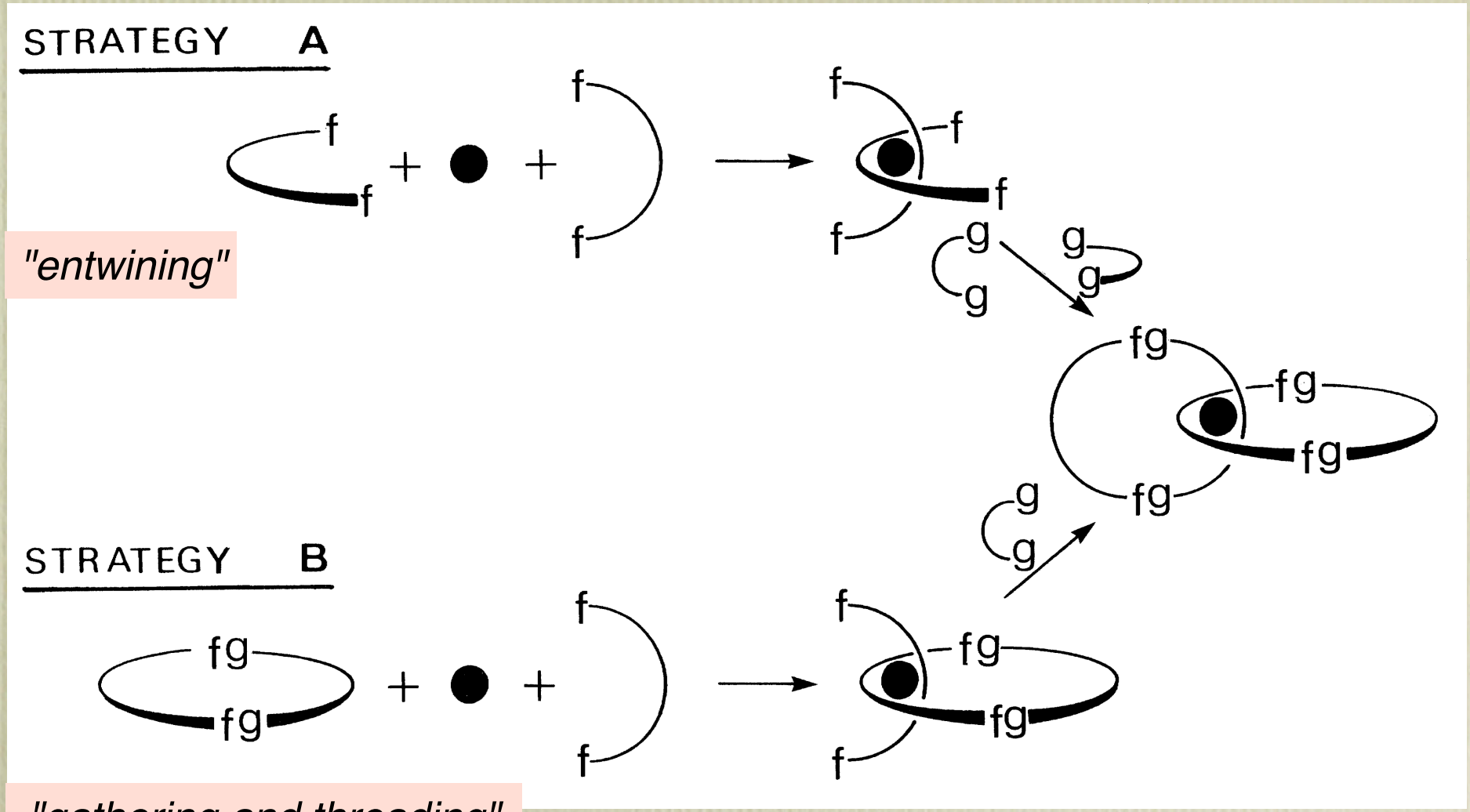
* * * *

Abstract : A new strategy has been developped for synthesizing catenanes; it is based on a generalized template effect, as shown in Figure 1. The first example of a novel class of molecules, the **metallo-catenanes**, has been obtained in good yield : it contains copper (I) and macrocyclic phenanthroline derivatives.

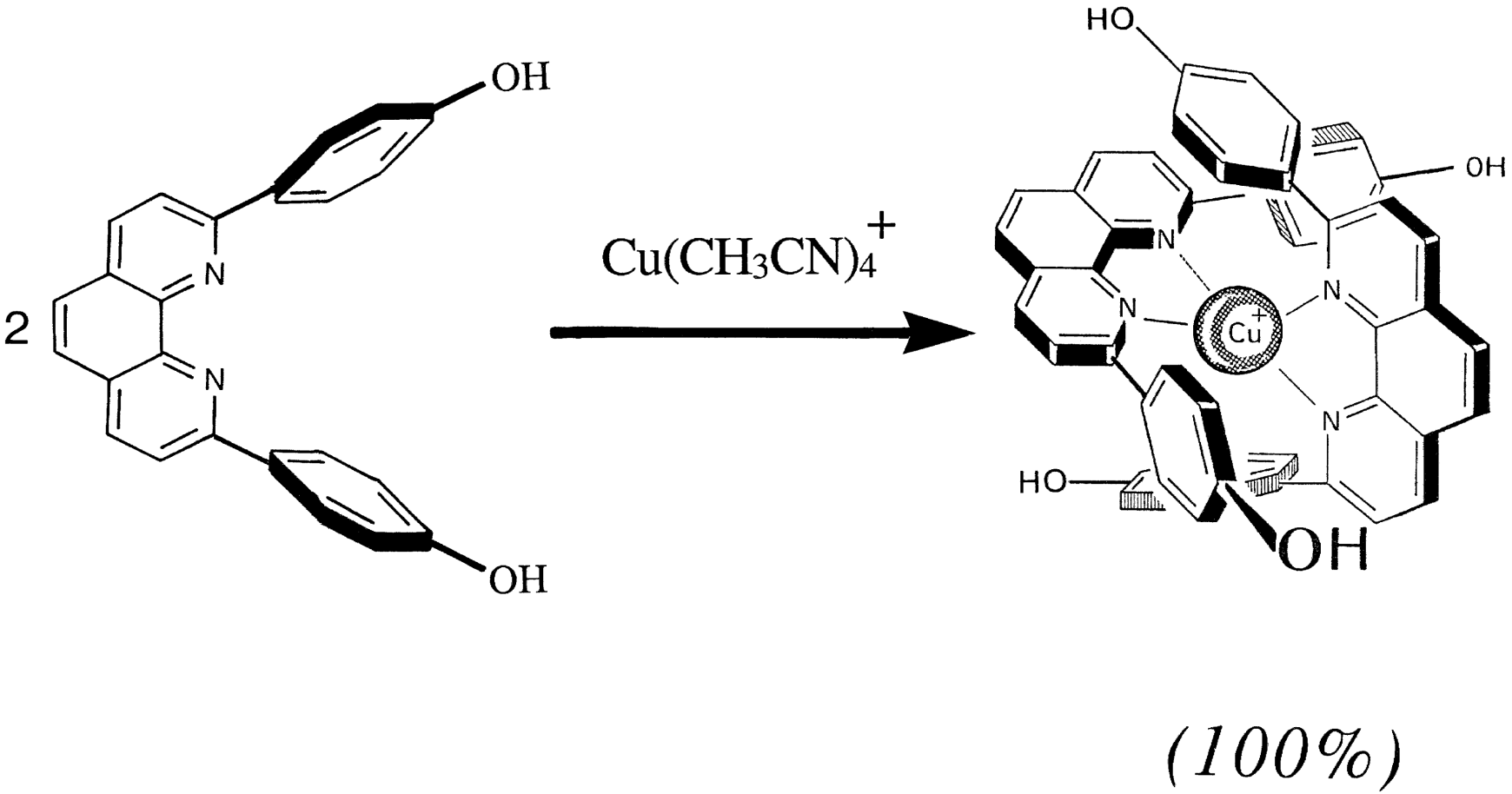
* * * *

Transition metal templated synthesis of a [2]catenane



Dietrich-Buchecker et al., Tet. Lett., 1983

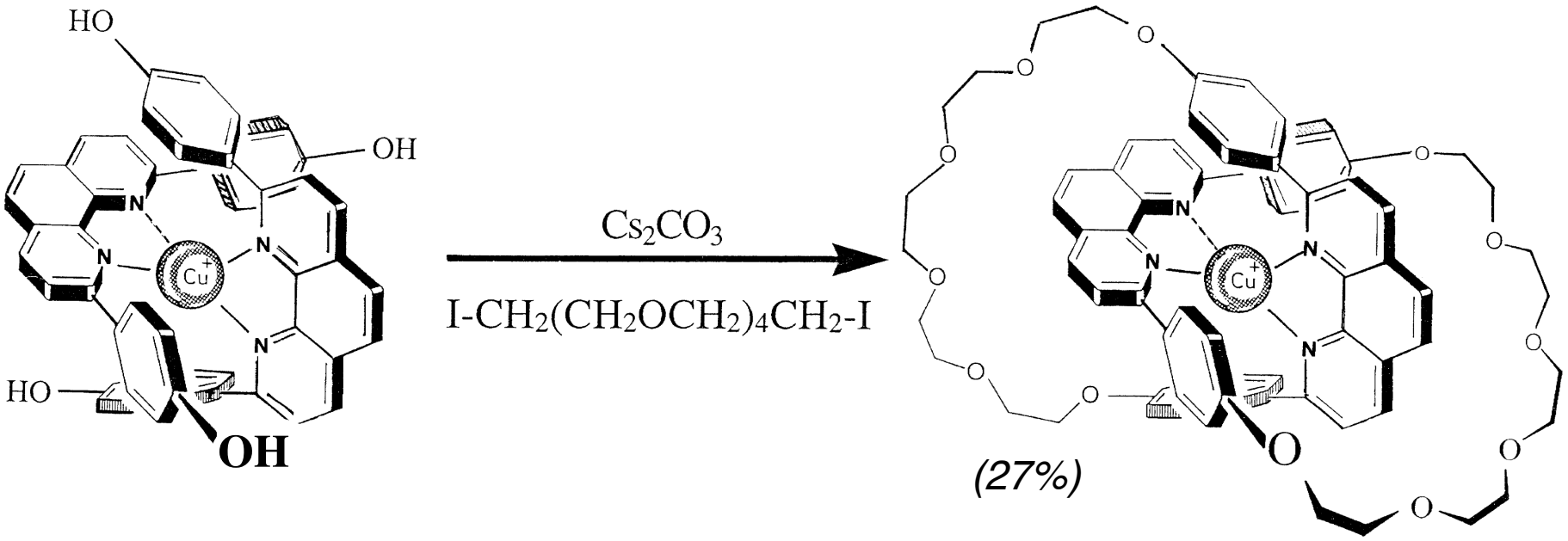
"entwining" two ligands around a copper(I) centre



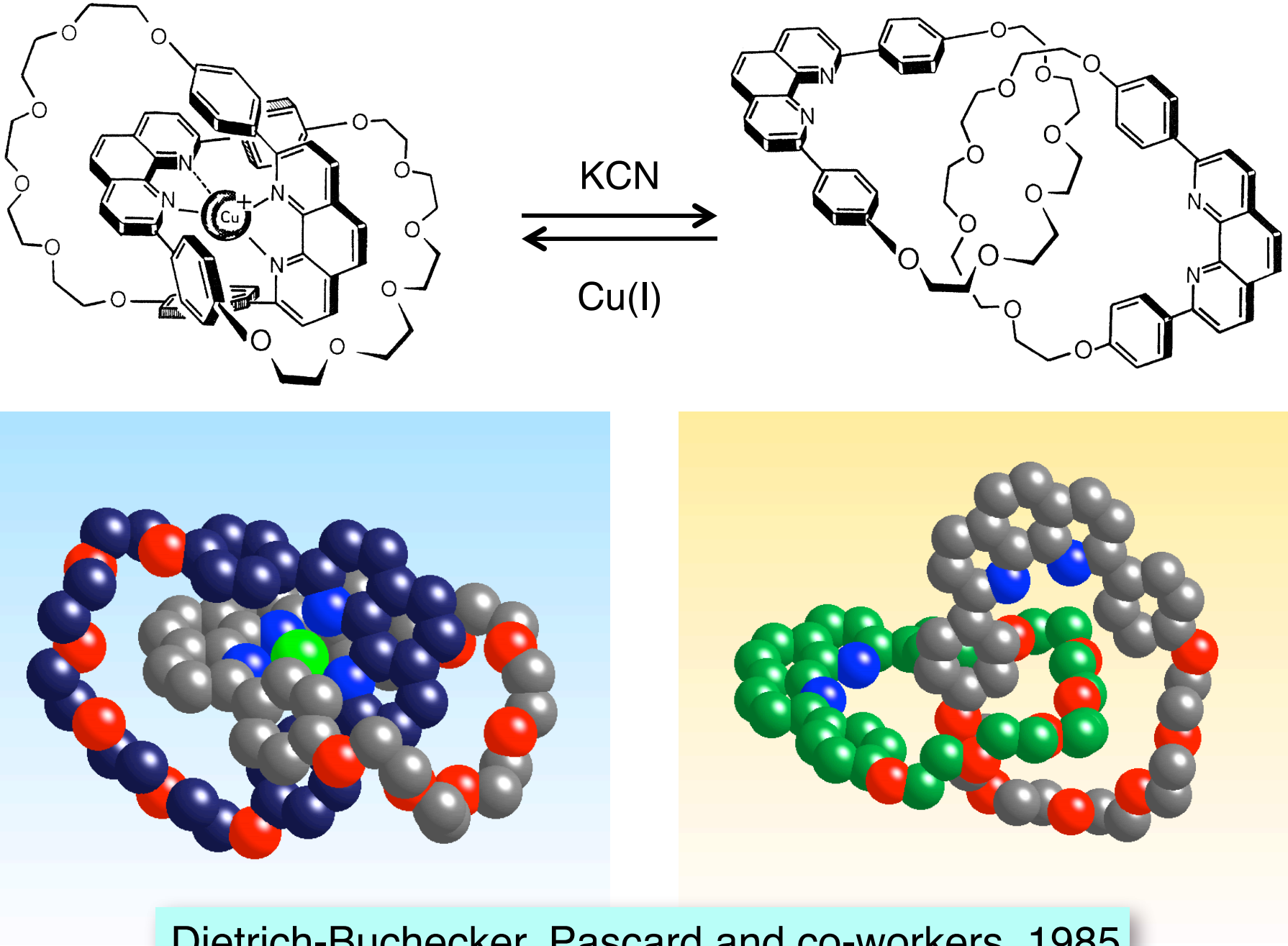
(100%)

Dietrich-Buchecker et al., 1983-1984

Double cyclisation reaction leading to the [2]catenane



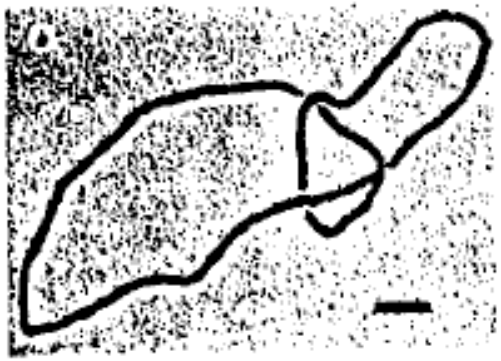
Dietrich-Buchecker et al., 1983-1984



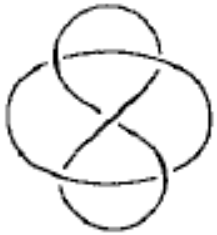
Dietrich-Buchecker, Pascard and co-workers, 1985

Catenanes and Knots are very common in biology : proteins, DNA, viruses

(a)



(b)



Electron micrographs of gyrase-produced **DNA catenanes** and **knots**: (a) trefoil knot; (b) figure-eight catenane

Synthesis of Catenanes : "template" methods

➪ Fraser Stoddart and co-workers : □□□ stacking and H bonds (1989)

➪ Chris Hunter : H bonding (1992)

➪ Fritz Vögtle et al. : H bonding (1992)

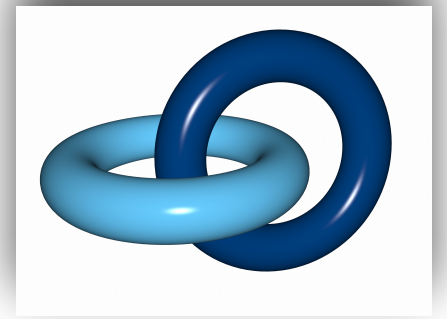
➪ Makoto Fujita et al. : kinetically labile Pd-N bonds and hydrophobic interactions (1994)

and, later on, many other outstanding research teams

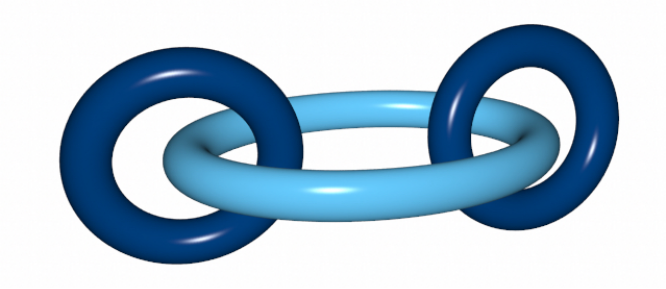
A pioneer in rotaxane chemistry :

➪ Hiroshi Ogino : threading of Cyclodextrins and stoppering *via* coordination chemistry (1981)

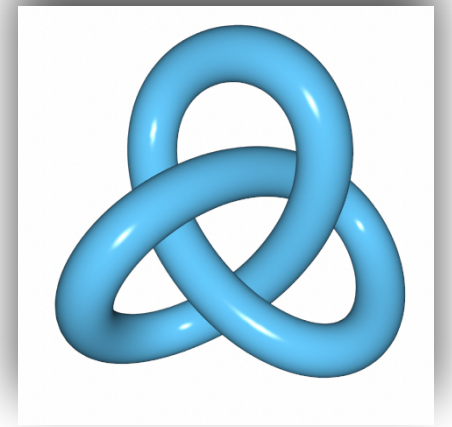
From a « simple » [2]catenane to more complex topologies



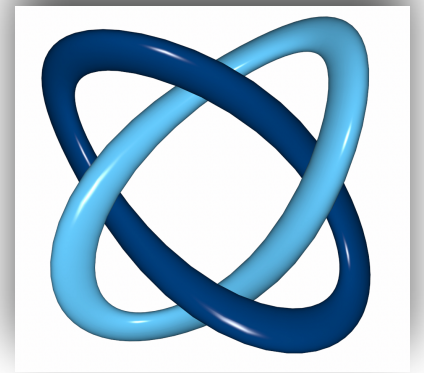
a [2]catenane (1983-1985)



a [3]catenane (1986-1987)



the trefoil knot (1989-1990)

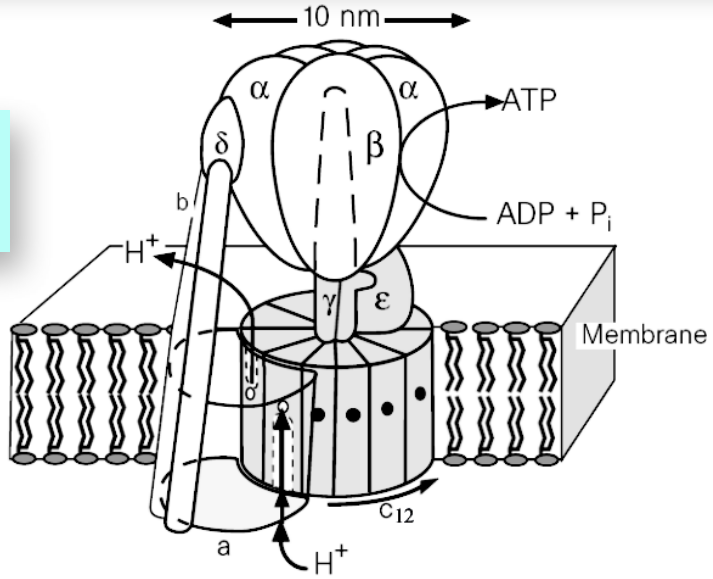


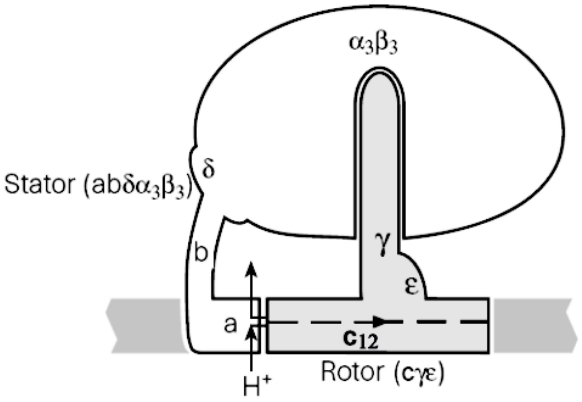
a doubly interlocking catenane (1994)

Molecular Machines

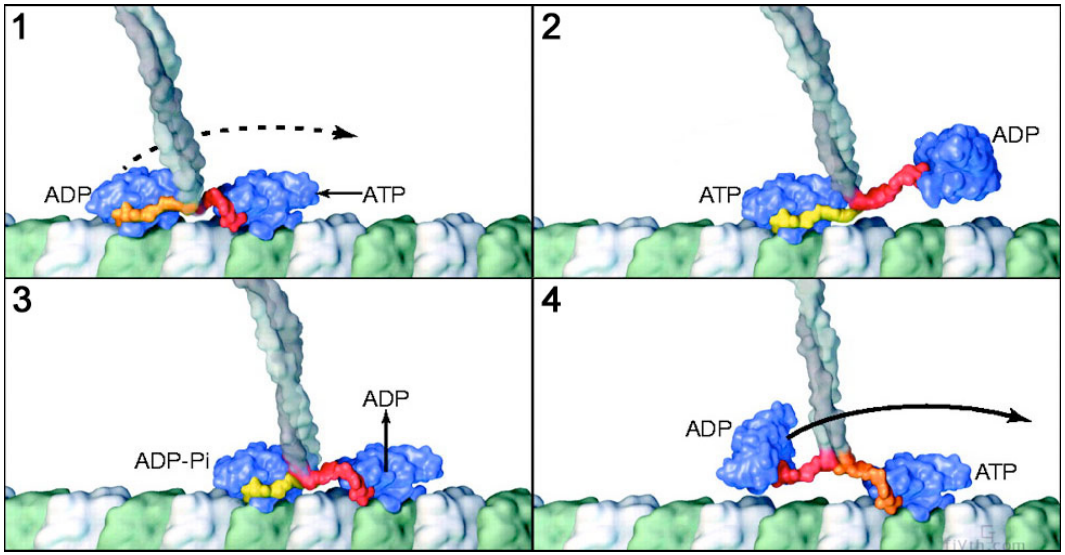
In biology, molecular motions are ubiquitous and vital. Two examples of biologically essential molecular machines

ATP-synthase : rotary motor

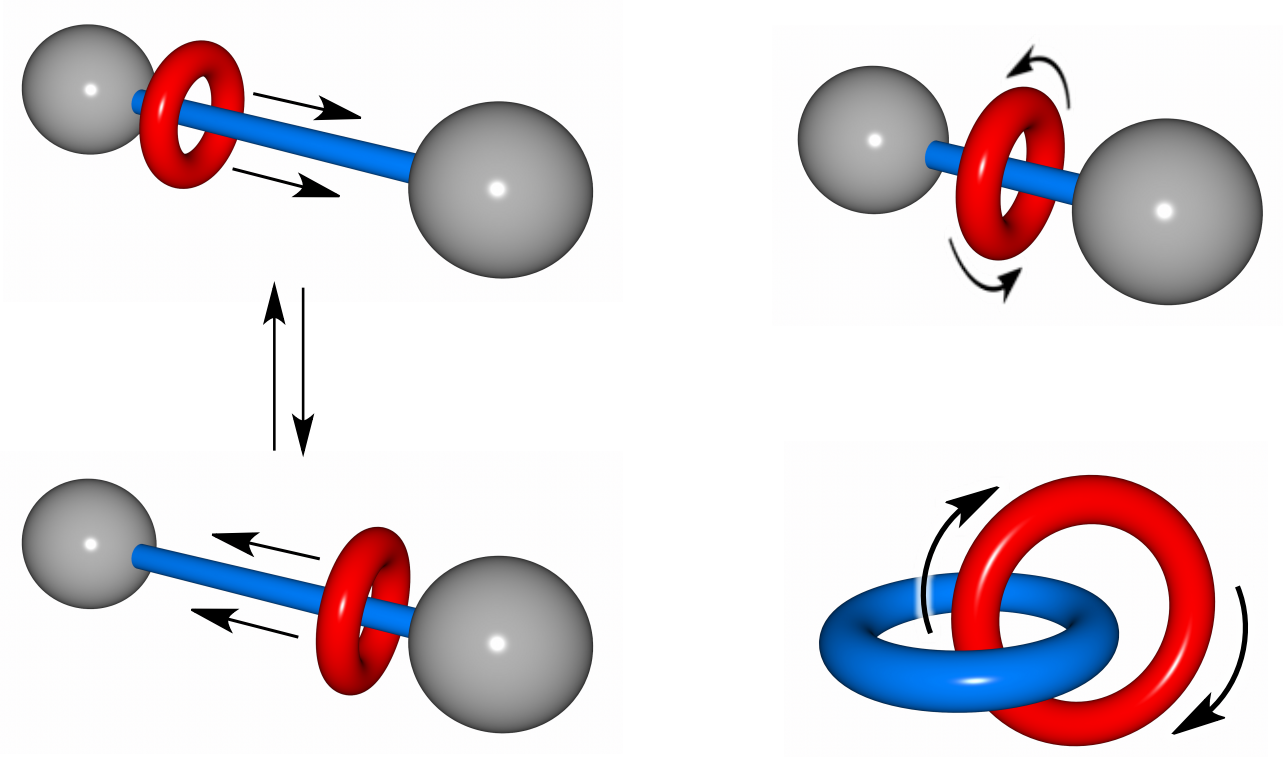




Kinesin "walking" on a microtubule : molecular shuttle

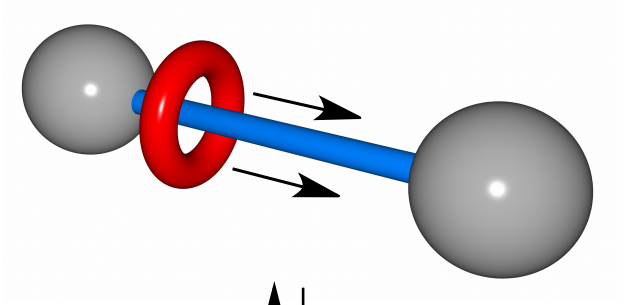


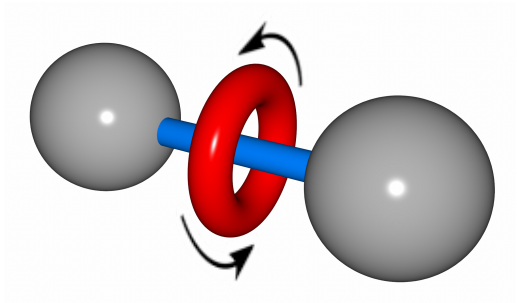
Catenanes and Rotaxanes in motion : Towards Molecular Machines

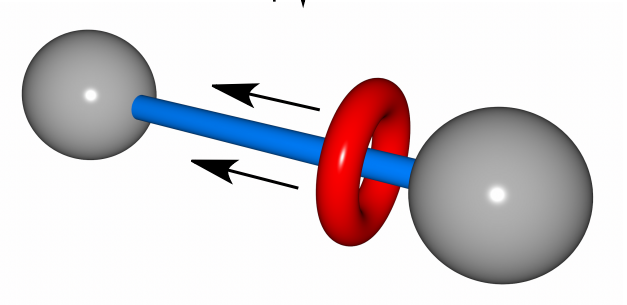


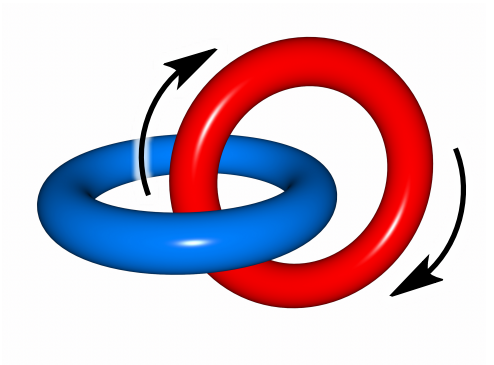
Catenanes and **Rotaxanes** are very well adapted to large amplitude motions : a ring can glide along the axis on which it is threaded (linear motor); it can also «pirouette» around the axis or within another ring

Catenanes and Rotaxanes in motion : Towards Molecular Machines



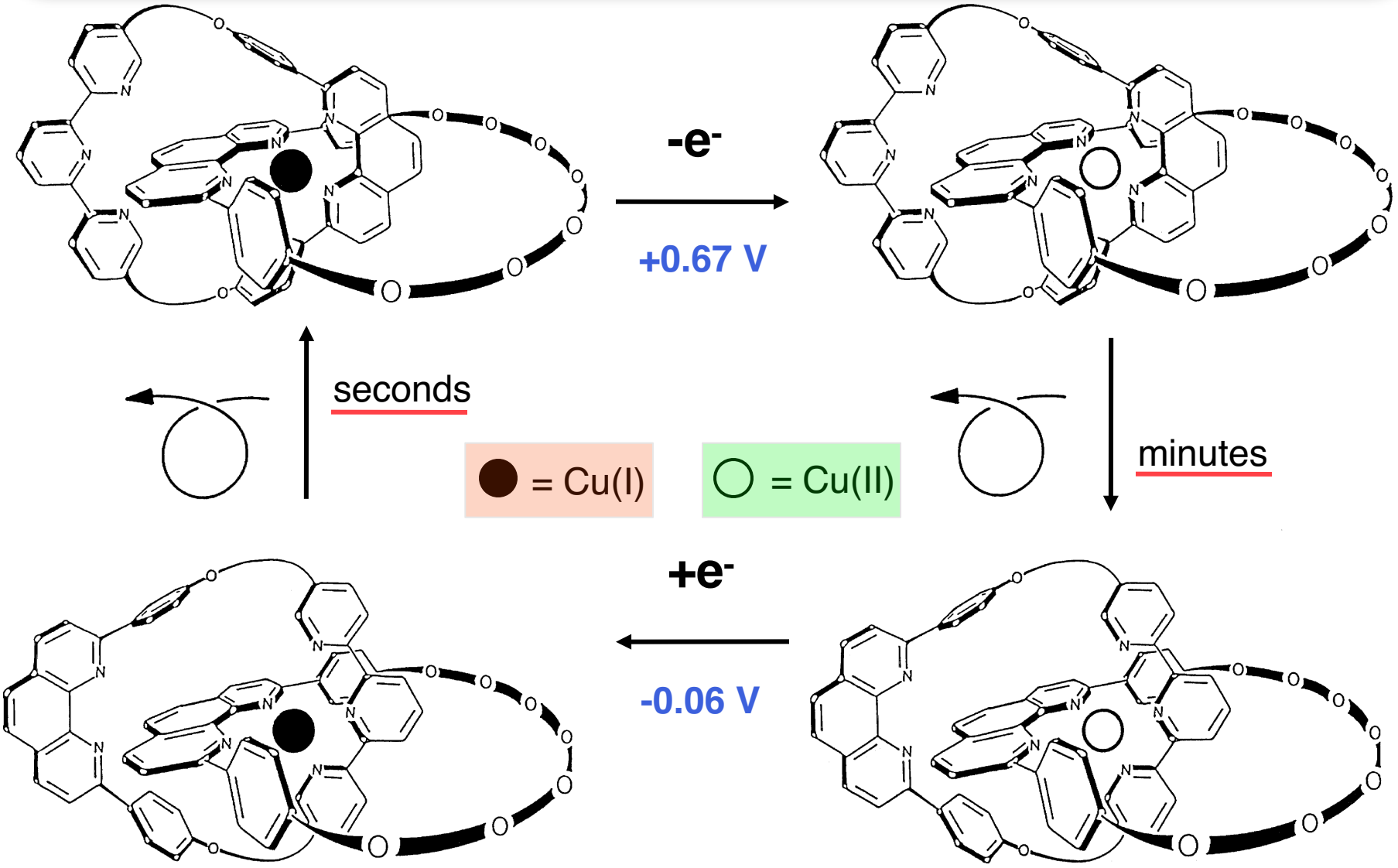


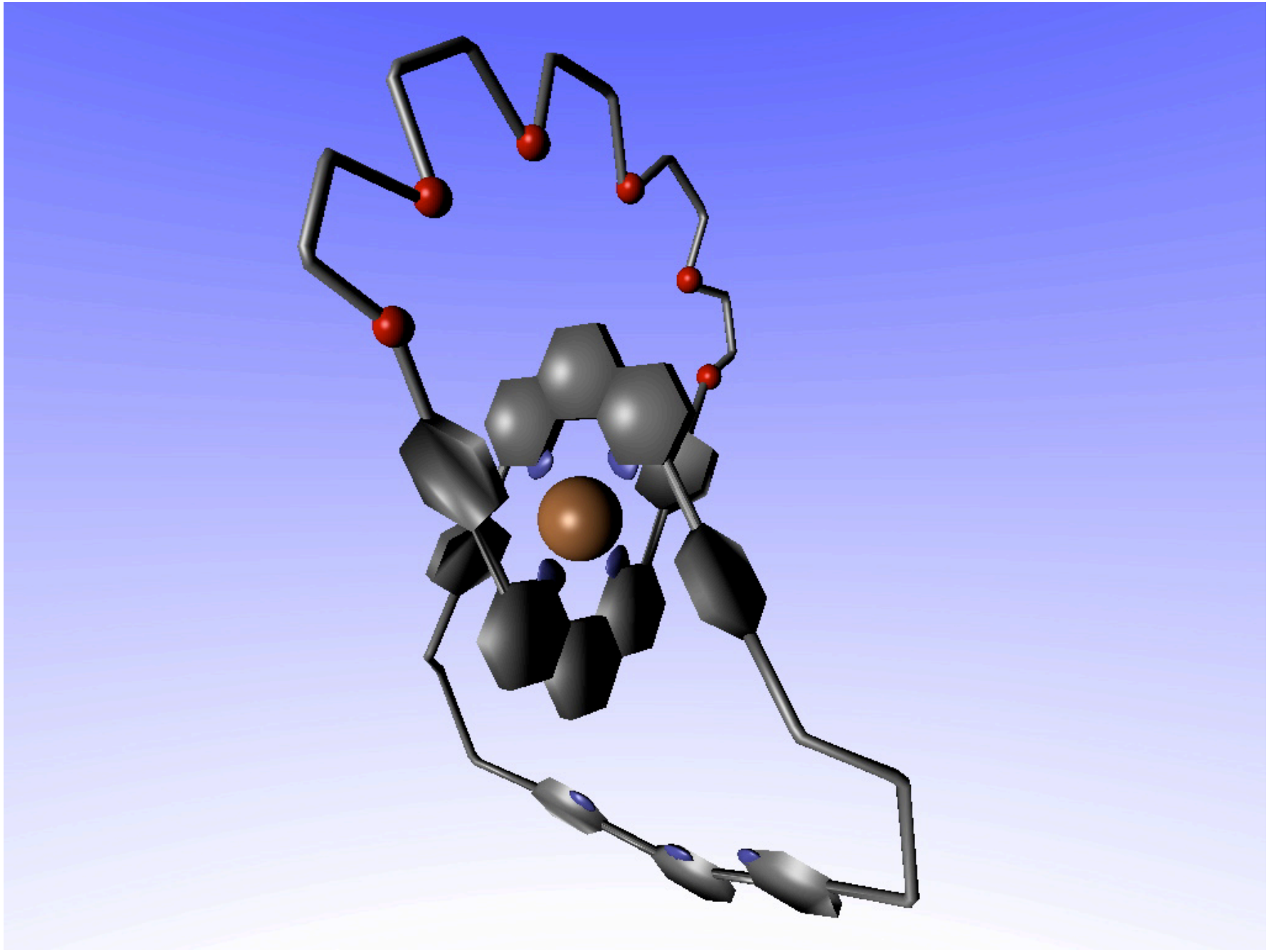




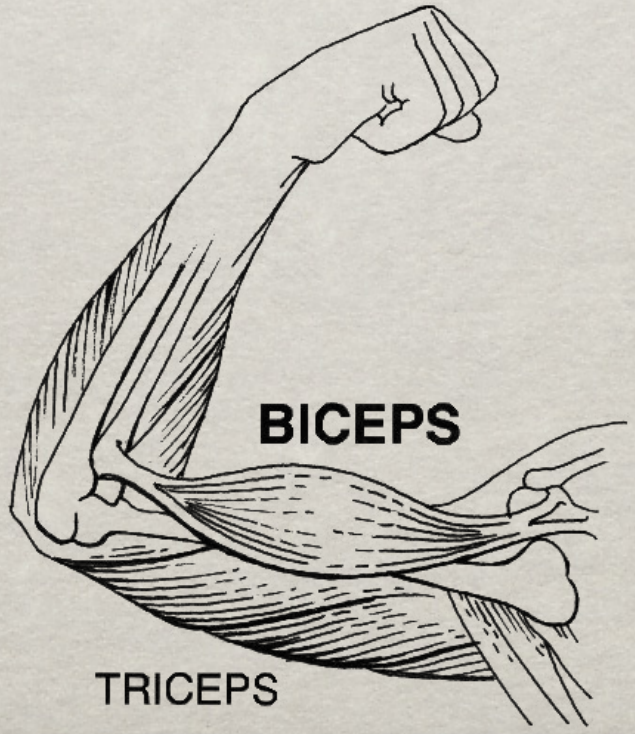
Stoddart - Balzani - Harada - Leigh - Nakashima - Beer - Coutrot - Easton - Huang - Flood - Giuseppone - Loeb - Nolte, Rohan and many other very creative research teams

rotation of a ring within another ring (**no directionality**): use of the Cu(II)/Cu(I) couple (*Livoreil et al., 1994*)
Real rotary motors : ***B. Feringa**, 1999*

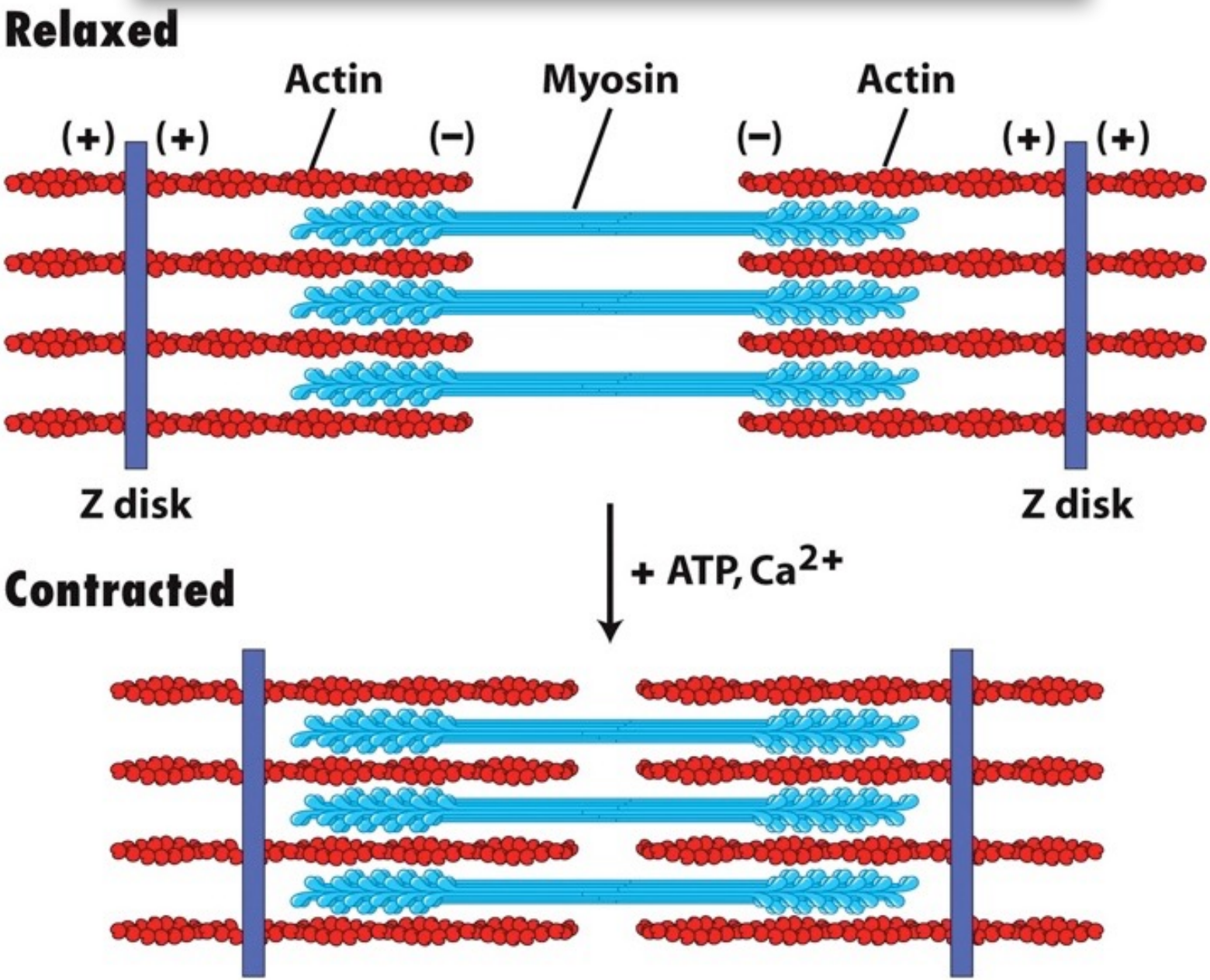




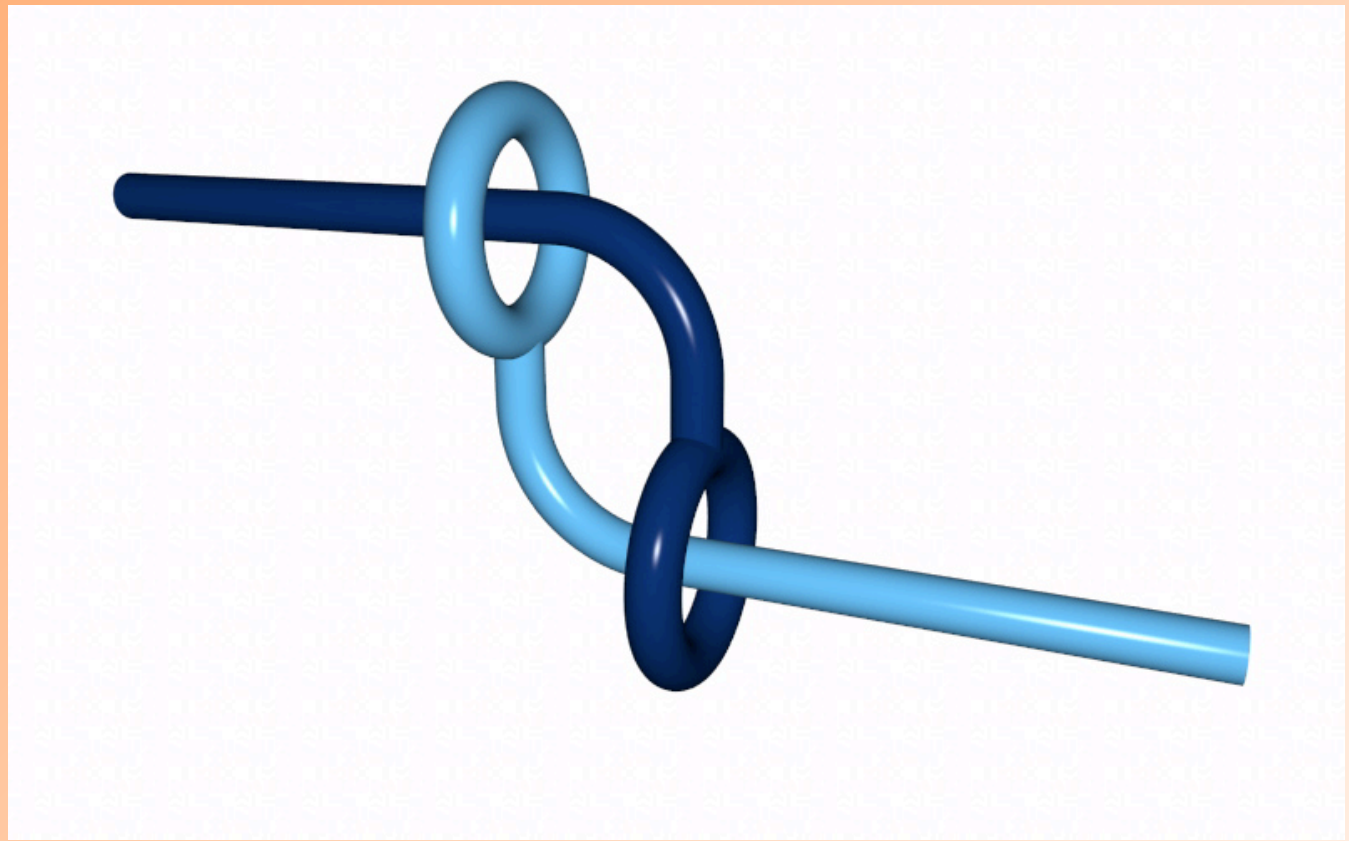
Contractile and extensible molecular systems : Towards artificial muscles



contraction and extension of a sarcomere
(elemental unit of the striated muscle)



A synthetic "molecular muscle" [2]rotaxane dimer



Maria Consuelo Jiménez (Chelo)...Christiane Dietrich-Buchecker

The dual function of transition metals :

1. Interlocking ring compounds can be obtained by using transition metals able to gather and dispose in a precisely defined geometry the various organic fragments to be incorporated in the target molecule

2. The presence of transition metals provides the systems with ***electrochemical*** *or* ***photochemical*** *properties which allow to set given fragments of the molecule in motion and thus to obtain molecular machines :*

Two or three state swinging [2]catenanes, two- or three-station molecular shuttles, « wing-flapping » rotaxanes, contractible and extensible molecules reminiscent of muscle, switchable receptors and molecular compressors, light-driven shuttles and swinging catenanes, etc.

A huge « thank you » to the members of our team "Laboratoire de Chimie Organo-Minérale"

Members of our university or of CNRS:

Marc Beley
Christiane Dietrich-Buchecker †
Jean-Claude Chambron
Jean-Paul Collin
Valérie Heitz
Jean-Marc Kern †
Stéphanie Durot
Angélique Sour
Valérie Sartor

A special thought for our two first PhD students :
Pascal Marnot et Romain Ruppert

Catenanes, Rotaxanes and Knots

Laboratoire de Chimie Organo-Minérale (Strasbourg)

Christiane Dietrich-Buchecker - Jean-Claude Chambron - Valérie Heitz - Jean-Marc Kern - Jean-Paul Collin - Stéphanie Durot - Angélique Sour - Valérie Sartor

Jean Weiss - Abdel Khémiss - Dennis Mitchell - André Edel - Catherine Hemmert - Jean-François Nierengarten - Jean-Luc Weidmann - Gwénaël Rapenne - David Amabilino - Nathalie Solladié - Aude Livoreil - Riccardo Carina - Bernhard Mohr - Myriam Linke - Laurence Raehm - Maria-Jesus Blanco-Pillado - Neri Geum Hwa - Christine Hamann - Benoît Colasson - Pierre Mobian - Masatoshi Koizumi - Didier Pommeranc - Damien Jouvenot - Sylvestre Bonnet - Valérie Sartor - Benoît Champin - Julie Voignier - Fabien Durola - Oliver Wenger - Alexander Prikhod'ko - Pirmin Roesel - David Hanss - Yann Trolez - Julien Frey - Felipe Reviriego - Jacques Lux - Christian Tock - Maryline Beyler - Tomáš Kraus - Cécile

X-ray structures

Claudine Pascard - Michèle Césario (Gif-sur-Yvette) - Jean-Fischer - André De Cian - Nathalie Gruber - Richard Welter - Lydia Brelot (Strasbourg)

Kari Rissanen (Jyväskylä)

Catenanes and Rotaxanes in action

Aude Livoreil - Christiane Dietrich-Buchecker - Diego J. Cardenas - Jean-Paul Collin - Pablo Gaviña - Laurence Raehm - Jean-Marc Kern - Ingo Poleschak - Ulla Létinois - Jack Beierle - Maria Consuelo Jiménez (Chelo) - Anne-Chantal Laemmel - Antoine Joosten - Yann Trolez - Valérie Heitz - Pierre Mobian - Masatoshi Koizumi - Didier Pommeranc - Damien Jouvenot - Sylvestre Bonnet - Fabien Durola - Oliver Wenger - Alexander Prikhod'ko - Yann Trolez - Julien Frey - Felipe Reviriego - Jacques Lux - Christian Tock - Stéphanie Durot - Angélique Sour - Cécile Roche - Antoine Joosten

Light-induced motions - Collaboration with Bologna : Nicola Armaroli - Vincenzo Balzani - Lucia Flamigni - Francesco Barigelletti - Barbara Ventura

Contraction/Extension of a molecular figure-of-eight

Frédéric Niess and Vincent Duplan

My two first PhD students : Pascal Marnot and Romain Ruppert

Université de Strasbourg and Centre National de la Recherche Scientifique (CNRS)

European Communities, Région Alsace

International Center for Frontier Research in Chemistry
LabEx “Chimie des Systèmes Complexes”
Institut de Science et d’Ingénierie Supramoléculaires

Northwestern University, Evanston

My mentor and friend, **Jean-Marie Lehn**

Organo-Metallic Chemistry in Oxford with **Malcolm L. H. Green**

The teachers who had a strong influence on my scientific interests, **Guy Ourisson** and **Raymond Weiss**

My wife, **Carmen**, and our son, **Julien**

The two other laureates, **Fraser Stoddart** and **Ben Feringa**

Strasbourg,
the centre of Europe