From Chemical Topology to Molecular Machines

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Jean-Pierre Sauvage

a [2]catenane

The archetype of topologically non trivial (non planar) compound

Chemists have been interested in catenanes and rotaxanes for decades and decades. Unfortunately, these compounds were mostly hypothetical objects for discussions. They were considered as almost impossible to prepare

a [2]rotaxane

From Inorganic Photochemistry and Solar Energy to Catenanes, Rotaxanes, Knots and Molecular Machines

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

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

$Cu(dpp)_2^+$

The first practical synthesis of catenanes

copper(I)-templated synthesis of catenanes and knots

Christiane Dietrich-Buchecker (1942-2008)

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

UNE NOUVELLE FAMILLE DE MOLECULES : LES METALLO-CATENANES

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

(100%)

Dietrich-Buchecker et al., 1983-1984

Transition metal templated synthesis of a [2]catenane

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

Double cyclisation reaction leading to the [2]catenane

Dietrich-Buchecker et al., 1983-1984

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

a [2]catenane (1983-1985)

a [3]catenane (1986-1987)

the trefoil knot (1989-1990)

Solomon link : doubly interlocking catenane (1994)

strategy : from a [2]catenane to a trefoil knot

the trefoil knot

Cornelis Escher

Molecular knots in Strasbourg : Christiane O. Dietrich-Buchecker, Jean-François Nierengarten, Gwénaël Rapenne, Ricardo F. Carina

Molecular Switches and 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

Synthetic molecules are considered as **static** objects, even if they undergo **stochastic** (random) movements

By contrast, in biology **controlled** molecular motions are essential and **omnipresent** : rotary or linear motors, « walkers », systems undergoing contraction or extension, etc. **Motor proteins** are everywhere!

Th first molecular machine built on a [2]catenane

Pirouetting of a ring within another ring (**no directionality**)
(Livoreil et al., 1994 - EPR study : Kaim & Baumann, 1997)
Real rotary motors : *B. Feringa, 1999*

animation : Sylvestre Bonnet

Molecular «**shuttle**» : a ring glides along the axis on which it is threaded

two «stations» : a green one and a red one

A molecular "**shuttle**": the compound is set in motion by modifying the acceptor-donor interaction

Bissel, Córdova, Kaifer, Stoddart 1994

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

Animation : Jean-François Nierengarten

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

Molecular Compressors and Switchable Receptors

Molecular Compressors and Switchable Receptors

[4]rotaxane

Jean-Paul Collin, Fabien Durola, Julien Frey, Valérie Heitz, Felipe Reviriego, Yann Trolez and Kari Rissanen (*JACS*, **2010**); Cécile Roche & Angélique Sour (*Chem.Eur.J.*, **2012**)

Review article : *Acc. Chem. Res.*, **2014**

Before the emergence of « molecular machines », synthetic molecules were mostly considered as still objects or species undergoing stochastic movements. Molecular systems undergoing large amplitude motions in a controlled fashion were scarce

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 first two PhD students : Pascal Marnot and Romain Ruppert

Two-dimensional threaded arrays and adaptable receptor

Tomás Kraus (Strasbourg and Prague), Milos Budesinsky, Josef Cvacka (Prague)

Jean-Paul Collin*, Julien Frey, Valérie Heitz*, Efstathia Sakellariou, Christian Tock, Fabien Durola, Felipe Reviriego, Yann Trolez, Stéphanie Durot, Valérie Sartor, Angélique Sour, Benoît Champin and Cécile Roche

Bi-isoquinoline ligands and their complexes

Fabien Durola & Oliver Wenger, Pirmin Roesel, David Hanss,

Alexander Prikhod'ko, Jacques Lux

X-ray structures: André De Cian

Kari Rissanen et al. (Jyväskylä, Finland), Lydia Brelot (Strasbourg)

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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 Nobel laureates, **Fraser Stoddart** and **Ben Feringa**

In which field of application will the area of molecular machines and muscles be the most important in the future? It is today very risky to give an answer to this question. Presently, one of the most impressive extensions of molecular machines towards applications is concerned with "molecular computing" and electronic memory devices. The groups of Stoddart and Heath reported promising work in this area.

Many types of nanodevices and nanomachines can be envisaged in relation to chemical applications (for example, sorting and transporting molecules in solution or through membranes).

In the future, nano- and microrobots able to fulfil a large variety of functions (from medicine to everyday life) will have to be articulated. In a relatively long-term prospective, artificial muscles of various lengths (from microns to millimeters or even centimeters) might be needed for various applications such as humanoid robots, actuators for microfluidic science and technology, or prosthetic organs.

However, in spite of all the possibilities offered by molecular machines in terms of potential applications for the future, it should be stressed that basic research is still of utmost importance and is, or has been, at the origin of most of the technologies which are nowadays part of our daily life.