Molecular motors
Mechanized molecules

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Outline

History, motivations
Molecules, Synthesis
    Catenanes and Rotaxanes
Electro-optic Kerr effect
    Macrocycle rotation
Metal surface electric field testing
Applications

INTRODUCTION

SHUTTLES

BRAKES

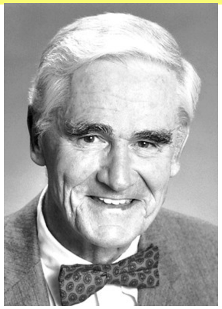
RATCHETS

Molecular architectures used
to restrict degress of freedom of movement
of submolecular components. Relative movement
via discrete large amplitude internal motions
Influence of External stimuli

KNOTS

Madre (smart) molekuly

Nobel Prize in Chemistry 1°987
Donald J. Cram; Jean-Marie Lehn & Charles J. Pedersen
"for their development and use of molecules with structure-specific interactions of high selectivity"



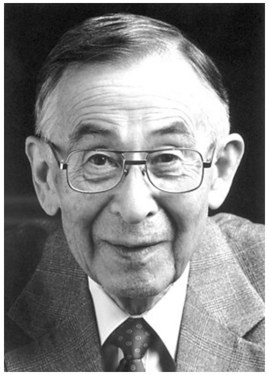
Donald J. Cram
1919 - 2001, University of Los Angeles, Ca, USA

Jean Marie Lehn 1939 –
Strasburg University; College de France

„Il n'existe pas de dogme en matière scientifique :
le chercheur ne croit pas, il pense »

W nauce nie ma dogmatu. Naukowiec nie wierzy lecz mysli

SUPRAMOLECULES



Charles J. Pedersen
1904 - 1989, Wilmington, Delaware

Nobel Prize in Chemistry 2016

"for the design and synthesis of molecular machines".

Jean-Pierre Sauvage, 1944 -
University of Strasbourg, Strasbourg, France

J. Fraser Stoddart, 1942 -

Northwestern University,
Evanston, IL, USA

Bernard L. Feringa, 1951 -
University of Groningen, Groningen, the Netherlands

EU Descartes Prize ceremony 2007

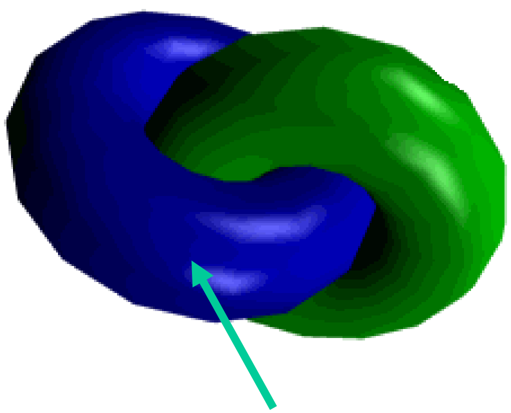
The European Descartes ceremony, Brussels 7 March 2007. From left to right: Claudie Haigneré, first French woman cosmonaute, member of Descartes Jury, David Leigh, University of Edinburgh (UK), Petra Rudolf (Groningen University, NL), Fabio Biscarini, CNR Bologna, Italy, Mojca Kucler Dolinar, Slovenian minister of Science and Education (Slovenia was exerting at that time the ruling presidency of EU), Janez Potočnik, EU Commissary for Science and Research, Francois, Francesco Zerbetto,University of Bologna, Italy, Jan Buma, University of Amsterdam, The Netherlands.

Goal

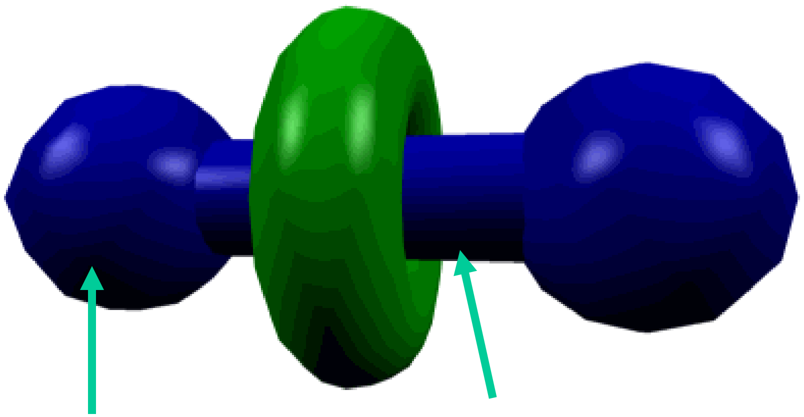
Design, synthesis and with external stimuli: electric DC, AC or optical field excite, control movements of molecular subparts to fulfill the desired functions

Molecules

a)



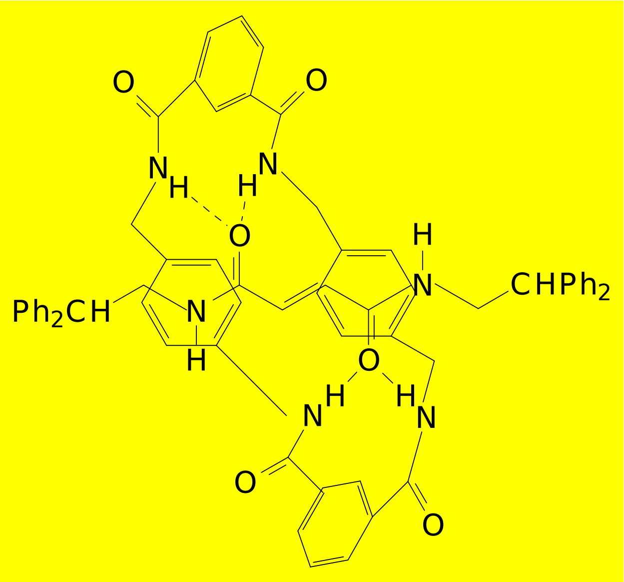
b)

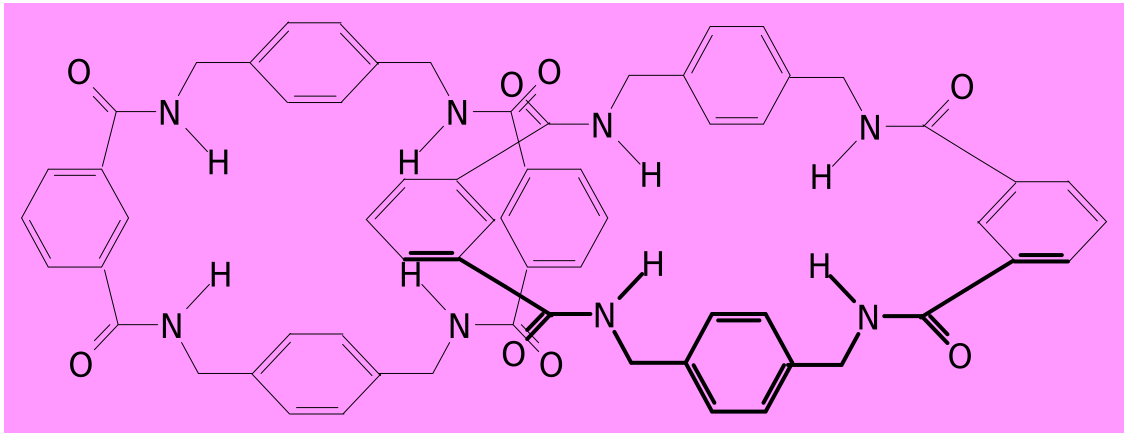


Catenanes

Rotaxanes

Molecules





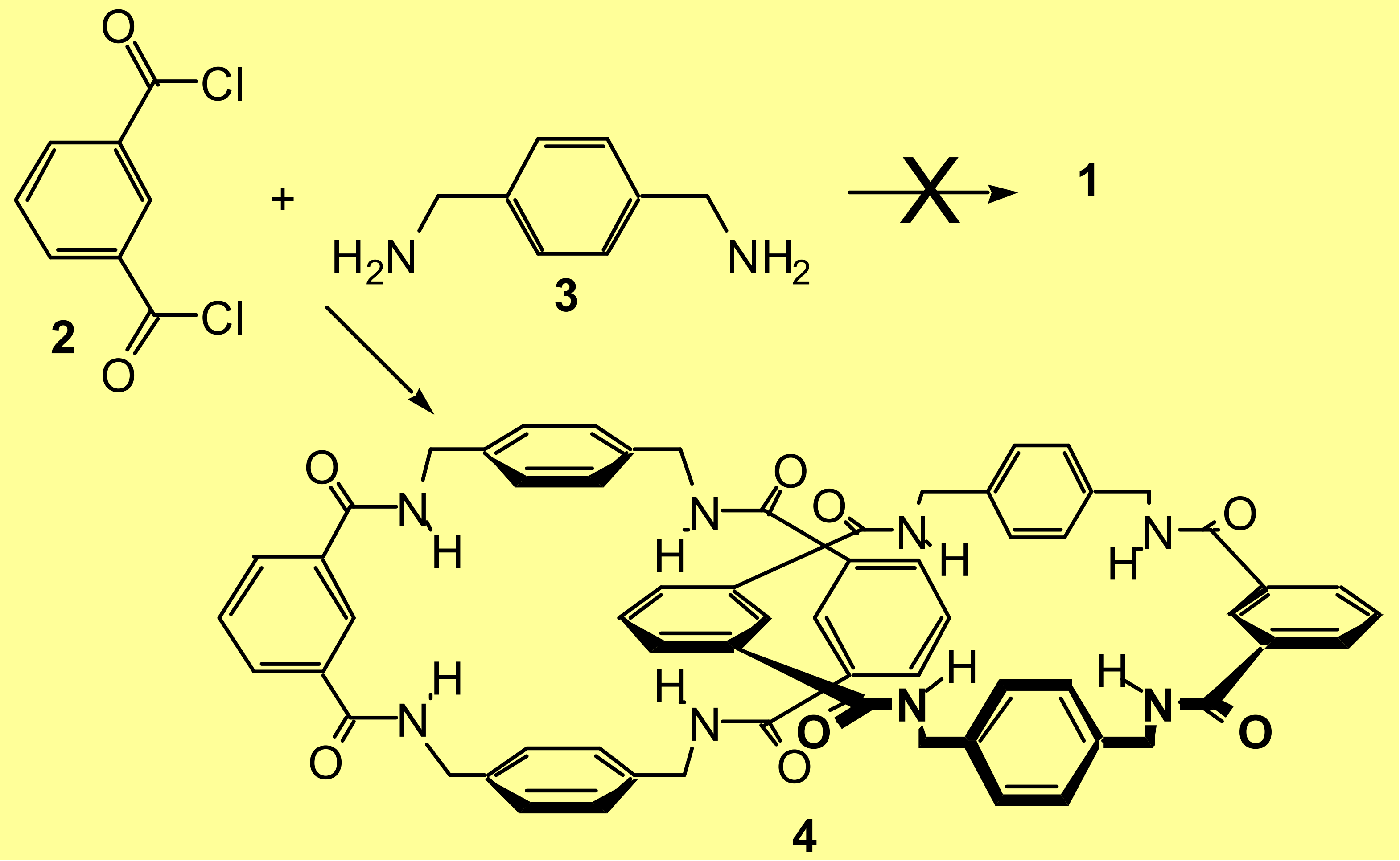
benzylic amide [2] rotaxane

benzylic acide [2] catenane.

Synthesis by the team from University of Edinburgh

Synthesis

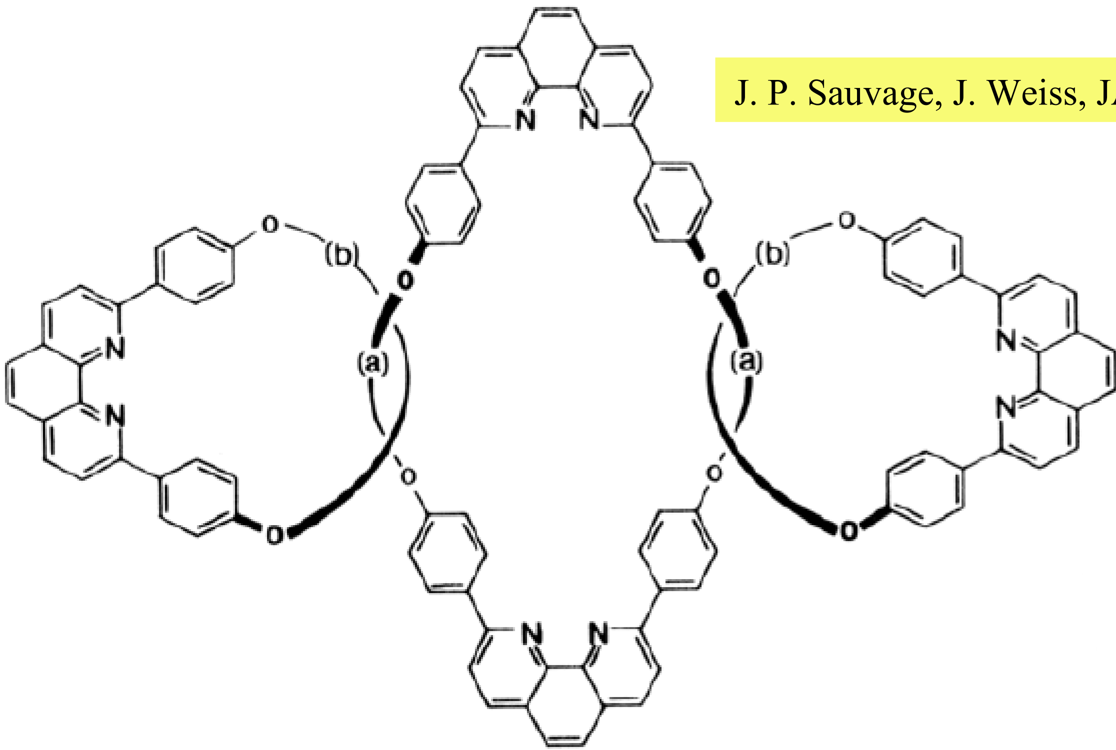
Catenanes



ÉCOLE NORMALE SUPÉRIEURE DE LYON

Tri ring catenane

J. P. Sauvage, J. Weiss, JACS, 107(21), 1985

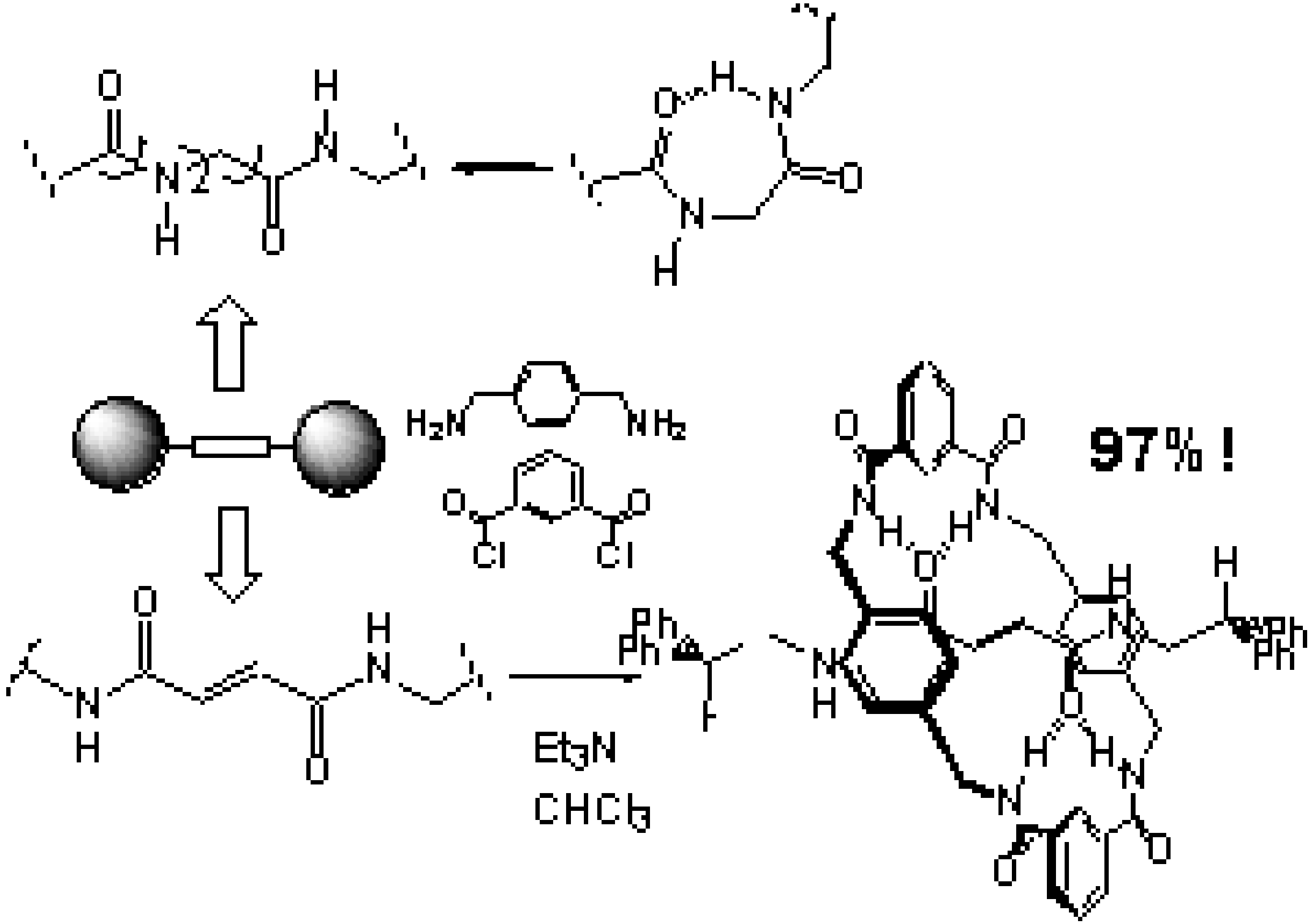


11 a = $CH_2(CH_2OCH_2)_2CH_2$, b = $CH_2(CH_2OCH_2)_4CH_2$

12 a = $CH_2(CH_2OCH_2)_3CH_2$, b = $CH_2(CH_2OCH_2)_4CH_2$

Synthesis

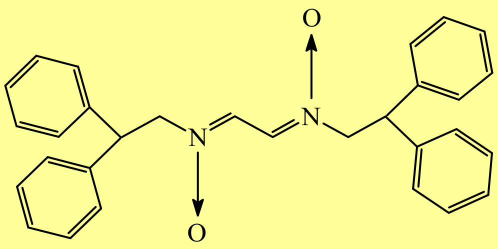
Rotaxanes



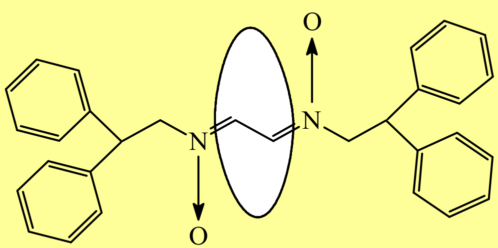
UNIVERSITATEA POLITEHNICA DIN BUCUREŞTI 1818

Rotaxanes

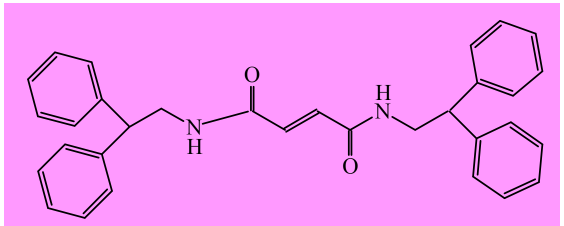
ÉCOLE NORMALE SUPÉRIEURE DE LYON



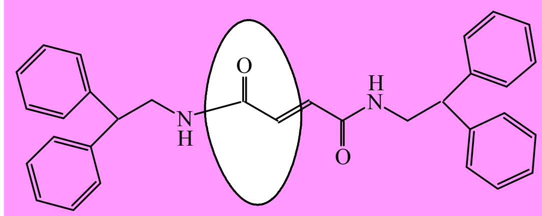
NOROT Thread



NOROT



FUMROT Thread

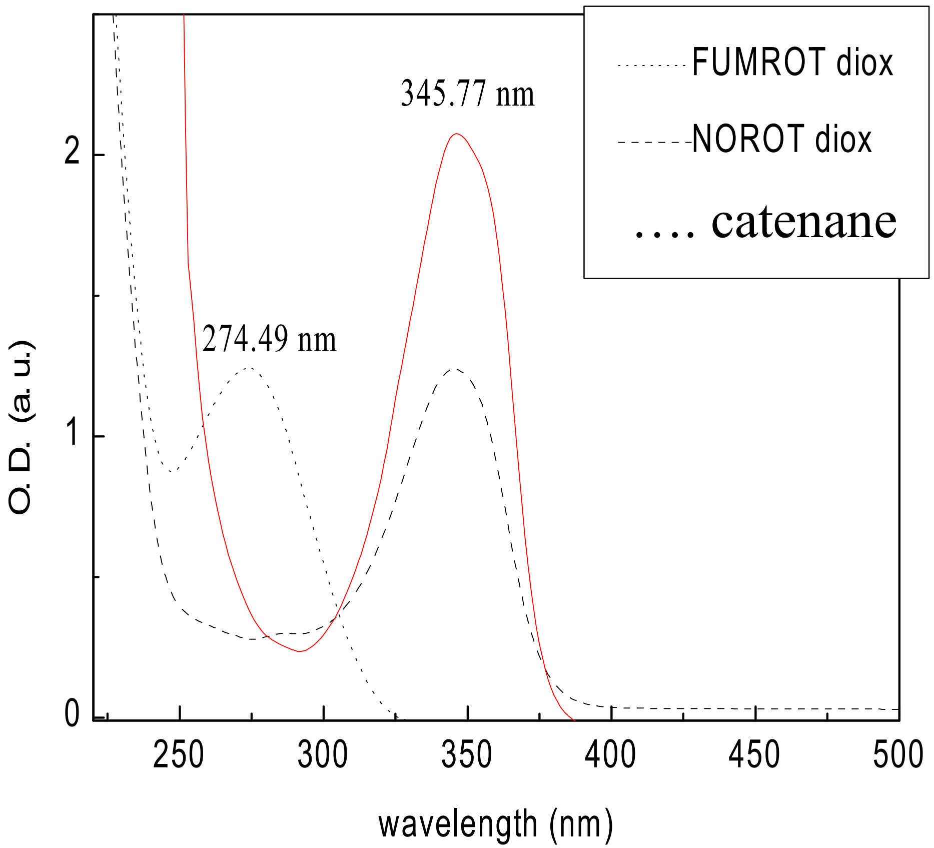


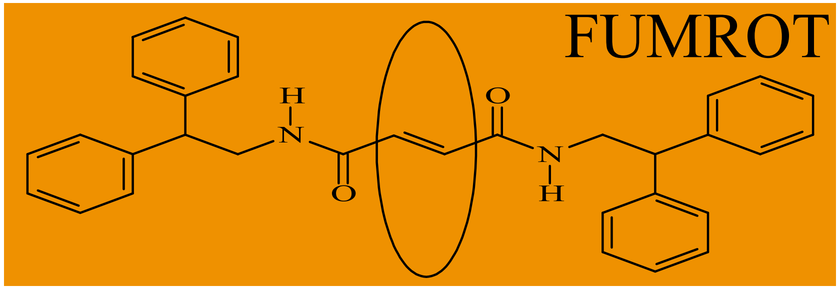
FUMROT

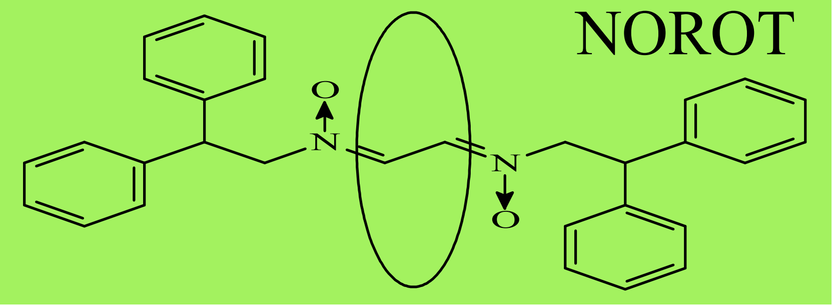
Polyrotaxanes

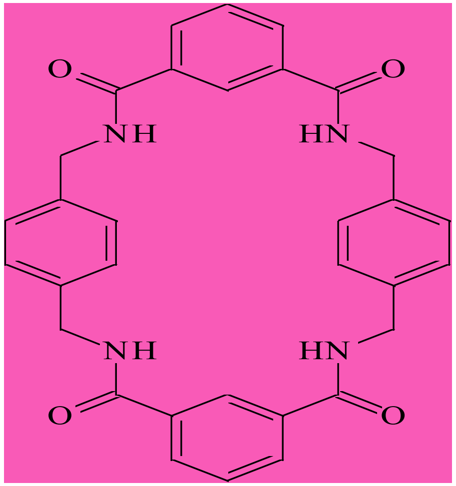
T. Lonjens, DSM

Absorption spectra









THIN FILMS

Thin films deposited on glass, silicon, silver, mica and fused silica substrates.

-Initial and final level of vacuum 10^{-6} and 10^{-5} Torr

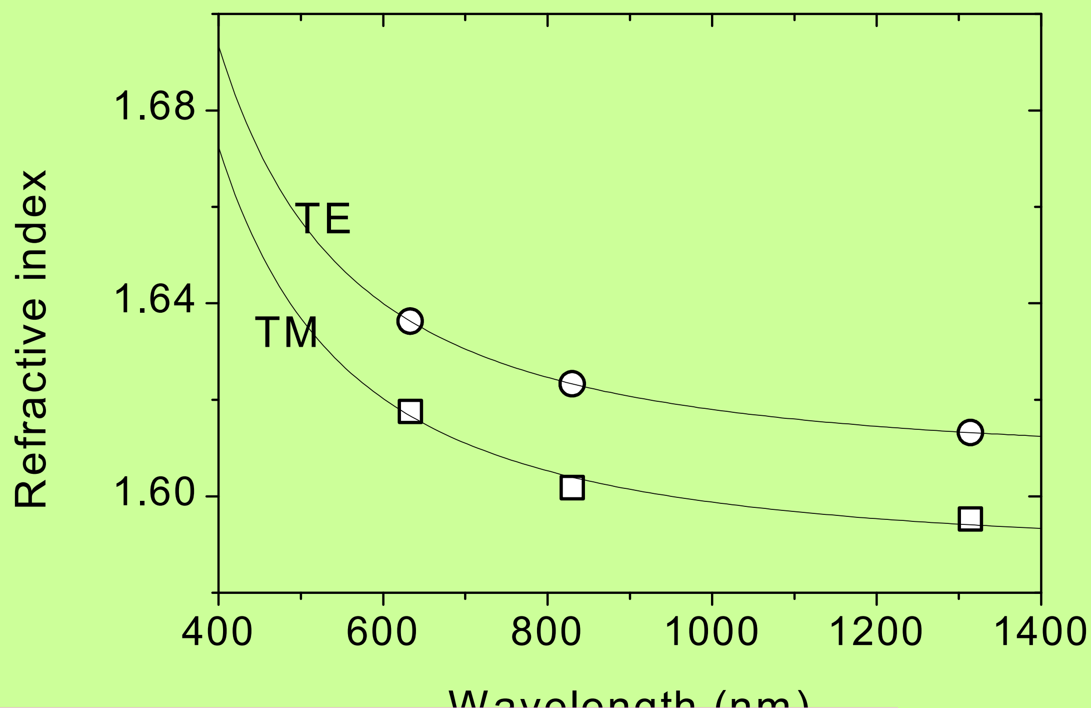
- Powder and target temperatures 220°C and 25°C.
- Deposition rate 30 to 10 A/s.

Good quality

Refractive index m-lines spectroscopy.

Thickness: m-lines spectroscopy when more than one guided more, and profilometry.

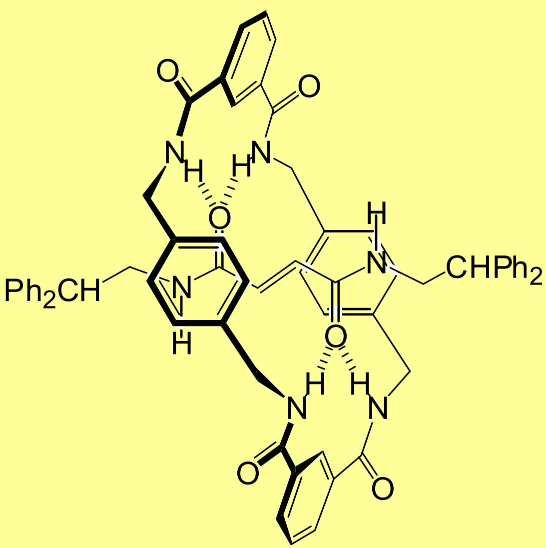
Thin films of CAT1



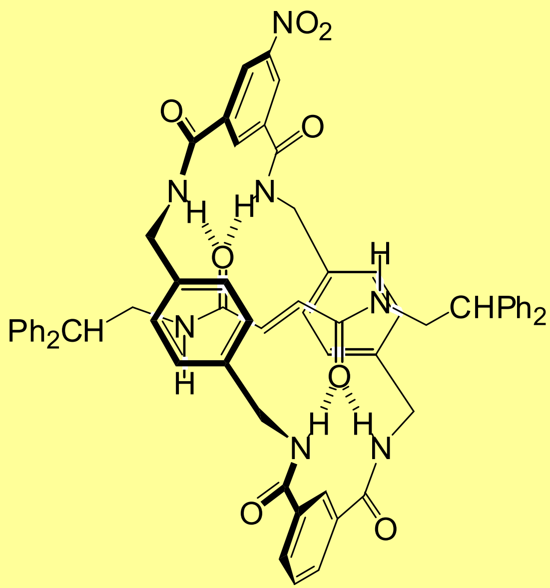
$$n^2 = 1.588^2 + 0.0333/(\lambda^2 - 0.198^2) \quad \text{(TM)}$$
$$n^2 = 1.610^2 + 0.0345/(\lambda^2 - 0.198^2) \quad \text{(TE)}$$

Functionalized rotaxanes with the nitro group

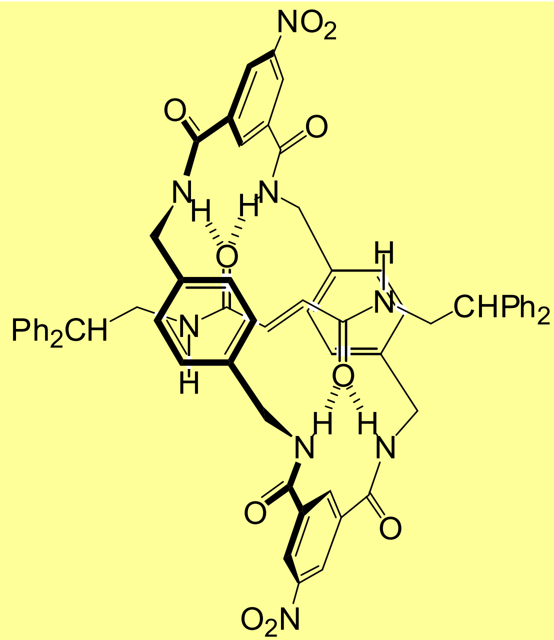
1



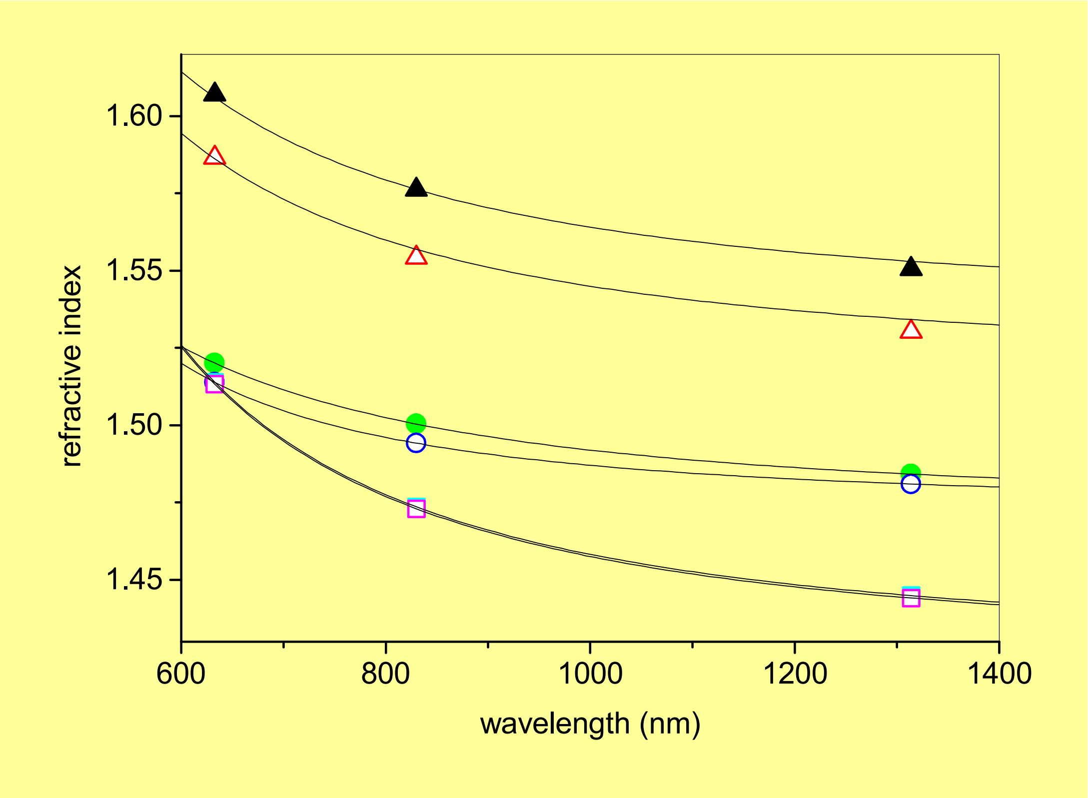
2



3



Control of order



rotaxane **1** - Δ, rotaxane **2** - O, rotaxane **3** - €

ELECTRO-OPTIC Characterization

The EO Kerr effect can be used to study the equilibrium and dynamic properties of molecules in solution by applying a DC or AC field, including optical electric fields (optical Kerr effect).

- The study possible for all molecules, with center of inversion (inducd dipole moment) or not
- The induced birefringence (change of the refractive index in direction parallel and perpendicular to E field) is proportional to the squar of the applied electric field

$$\left(\Delta n_{\perp} - \Delta n_{II}\right) = B\lambda E^2$$

EO Kerr effect

$$\left(\Delta n_{\perp} - \Delta n_{II}\right) = B\lambda E^{2}$$

$$B \propto \chi^{(3)}(-\omega_l ; \omega, -\omega, \omega_{el})$$

The produced phase shift:

$$\partial\phi = \Delta k l = \frac{2\pi}{\lambda} l\left(\Delta n_{\perp} - \Delta n_{II}\right) = 2\pi B l E^{2}$$

The signal can be sepated from disturbing light with a lock-in amplifier

$$\partial\phi = 2\pi B\lambda\left[\frac{1}{2}E^{2} - \frac{1}{2}E^{2}\cos 2\omega_{el} t\right]$$

Interest in application of AC electric fields

AC electric fields → adress molecular level structures

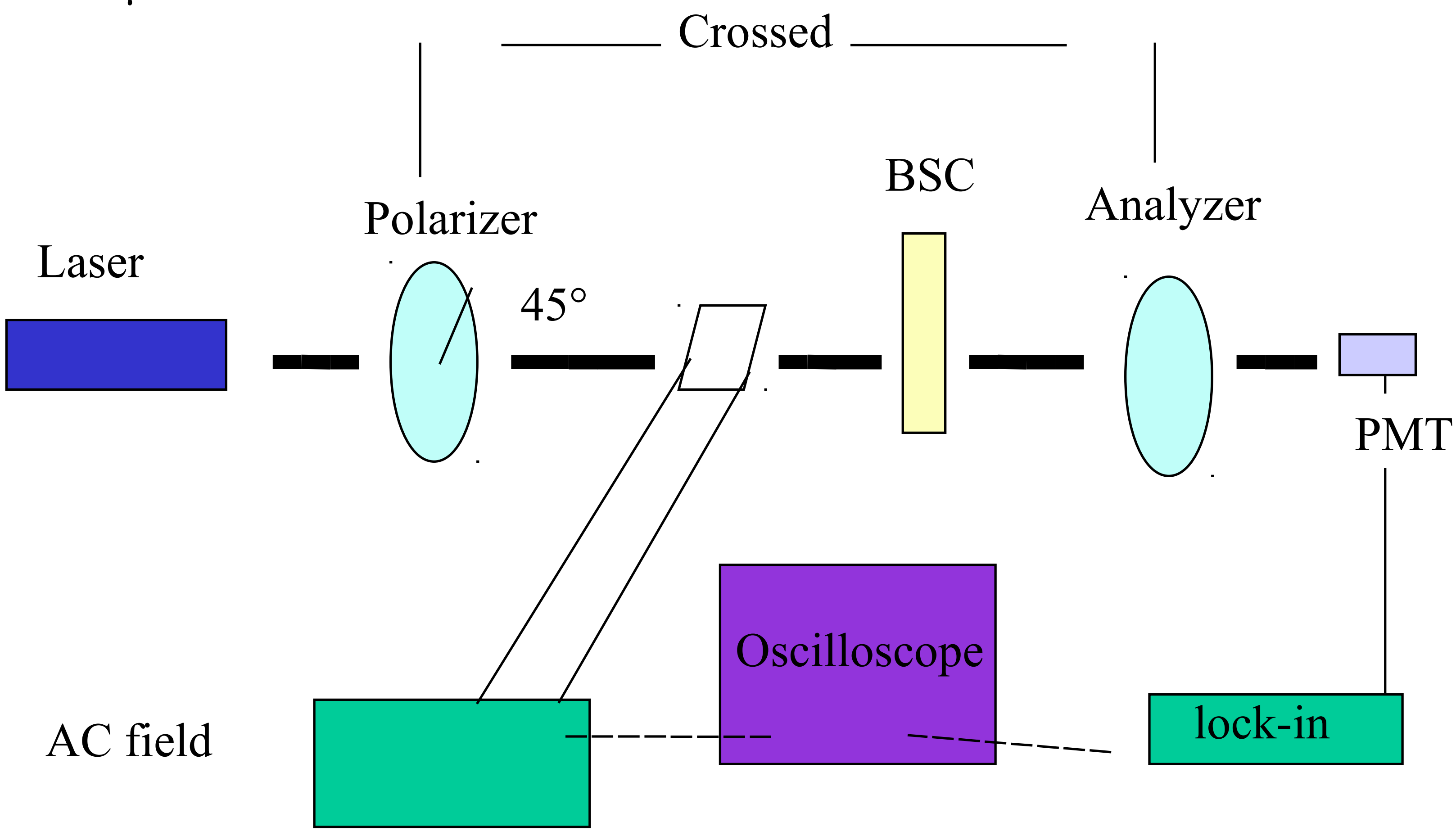
-probing electronic structures

-bring about the orientation of whole molecules (phenomenon exploited in liquid crystal displays).

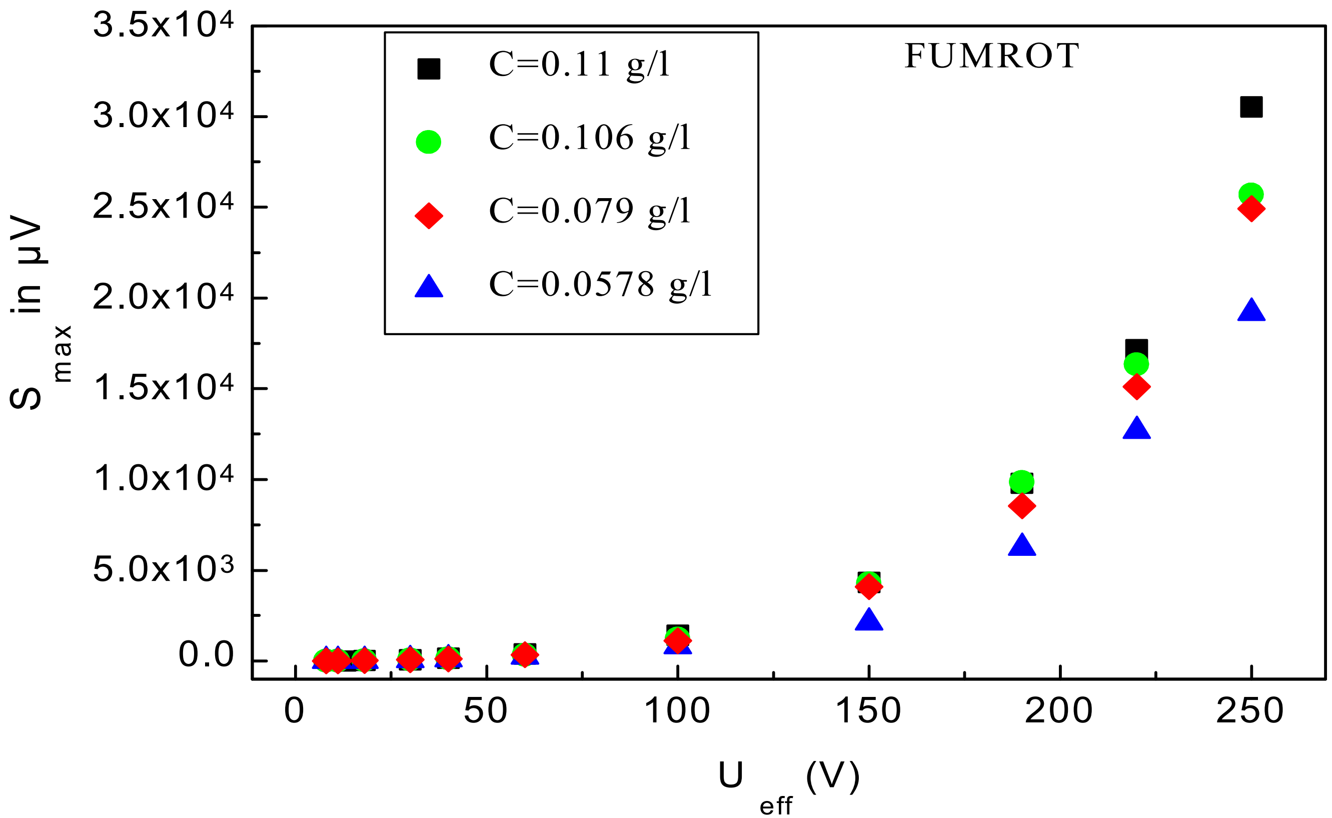
-interaction with large internal molecular motion

Electro-optic Kerr effect experimental setup

Cell 20µm

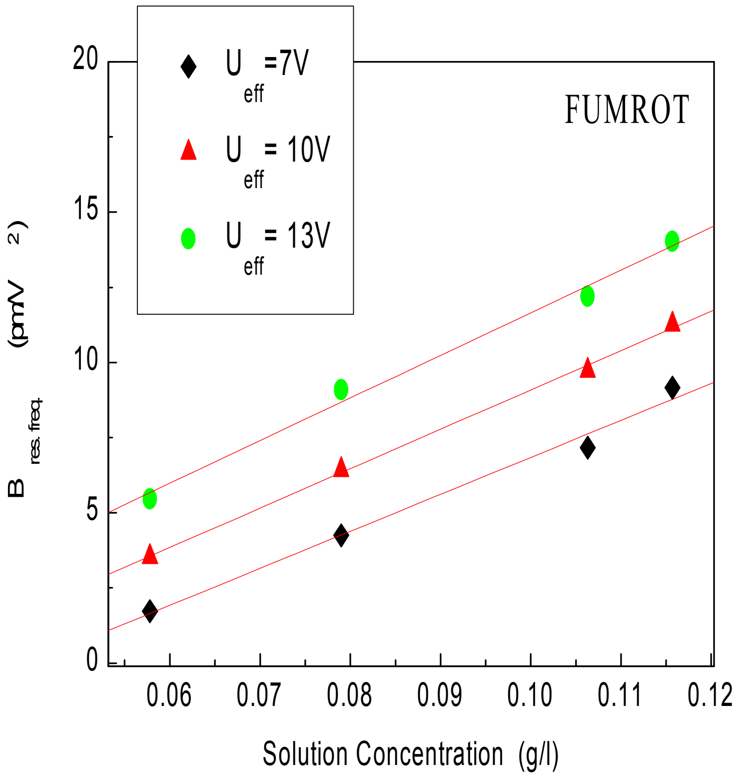


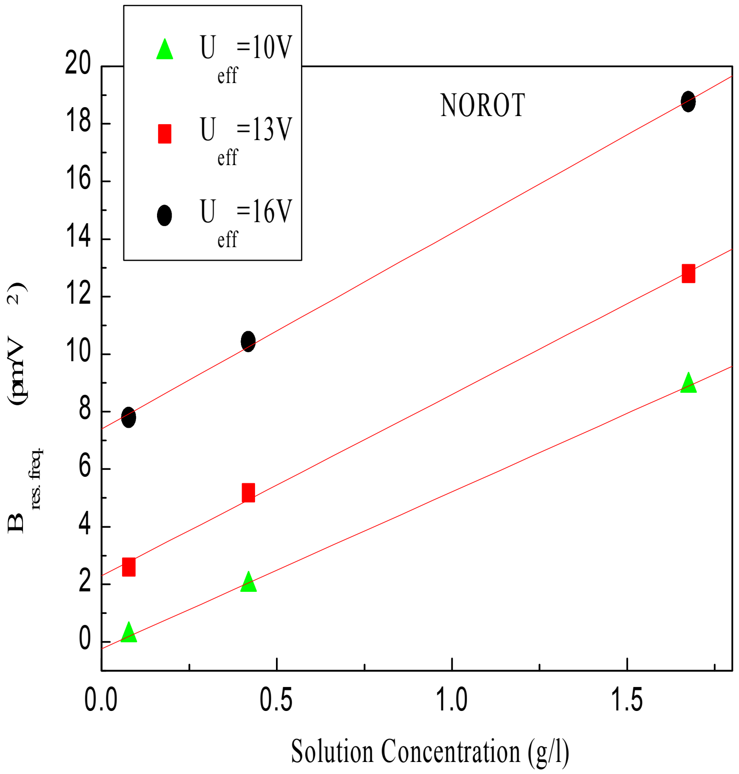
With U_{eff} (V)



LIST

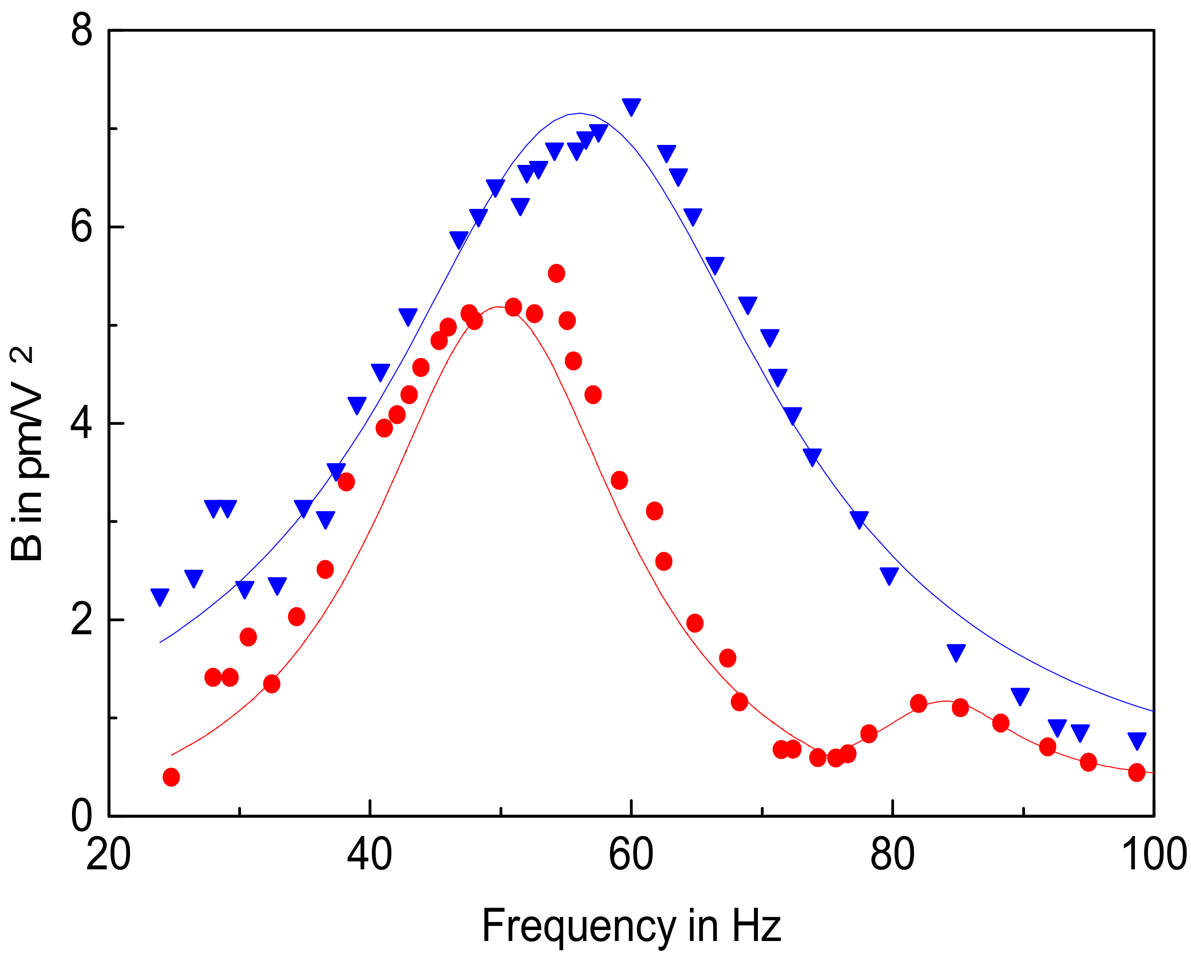
With concentration





LIST

Resonance frequency



DIOXAN

57.7Hz NOROT

53.3Hz FUMROT
83Hz

U_{eff}= 7V
E=0.35 V/μm

V. Bermudez, et al, Influencing Submolecular Motion with an Alternating Electric Field, Nature, 406, 608(2000)

VT ^{1}H NMR spectroscopy

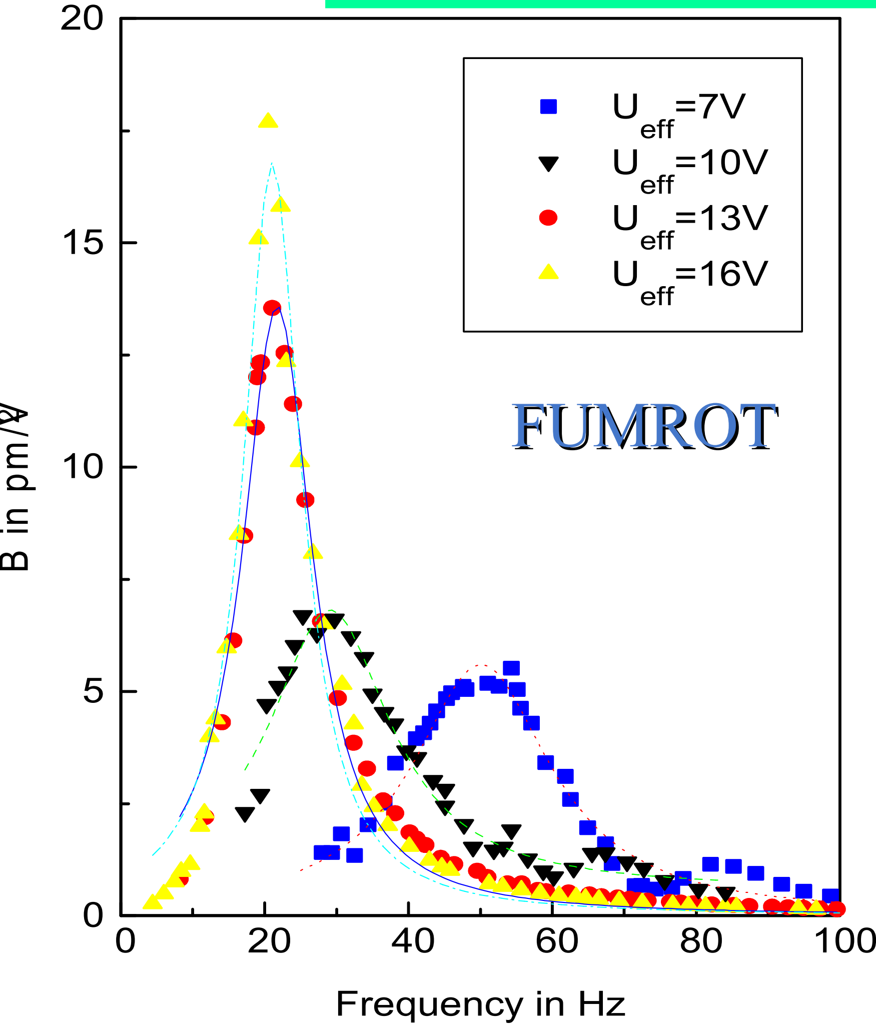
D. Leigh, Univ. Warwick, UK

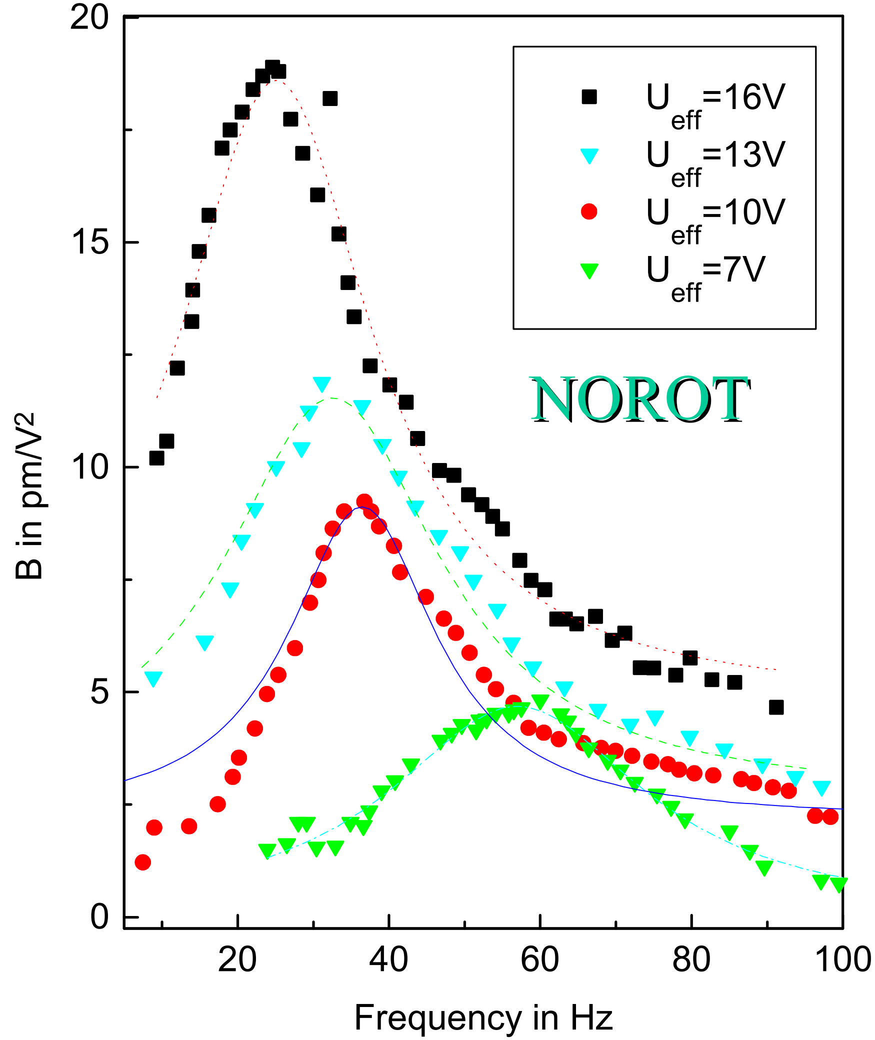
	E_a (kcal/mol)	K (Hz)	Motion
NOROT	12.2	405	pure rotation
FUMROT	13.4	340	more complex motion

Solvent: 80% 1.4 dioxane/ 20% $C_2D_2Cl_4$

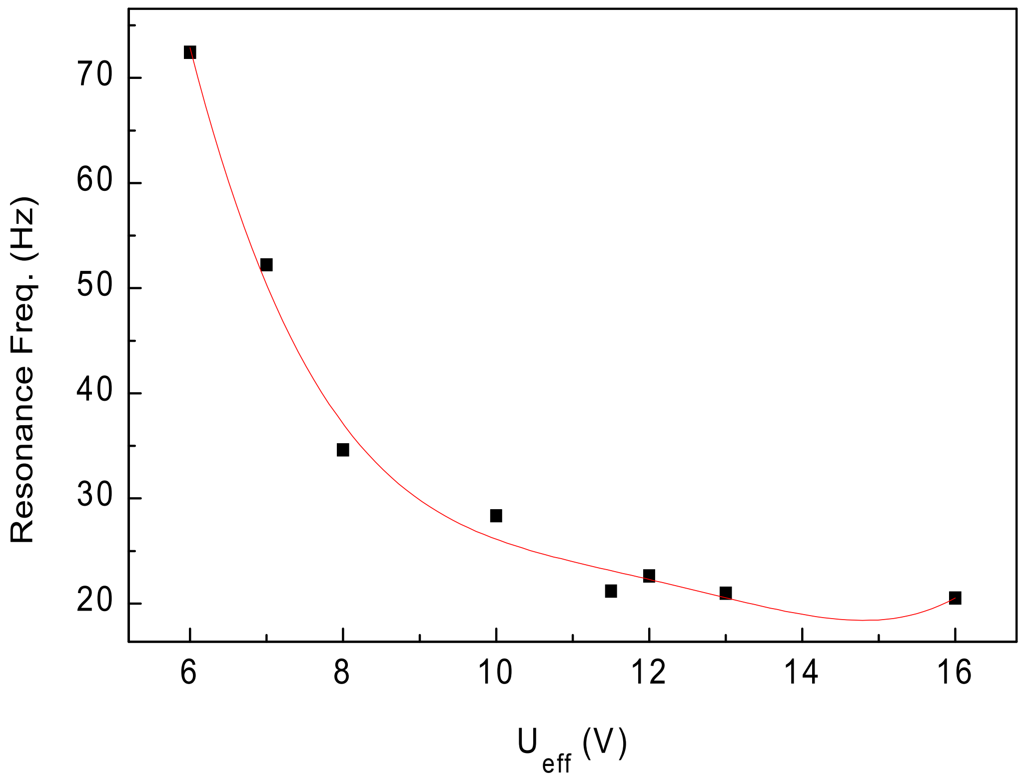
Simulation to understand what kind of motions

Applied Voltage





NMR and EO measurements



FUMROT

Extrapolating:

U_{eff} = 0V

Res. Freq. = 671 Hz

Agreement

MODEL

F. Zerbetto. Chemistry Dpt. Univ. Bologne. Italy

Molecular mechanics and dynamics
through the TINKER package
(http://dasher.wustl.edu/tinker)

MM3 force field
has already given good results
for rotaxanes and catenanes

Thermodynamics
to get activation energies and ΔG

RESULTS

E_a (kcal/mol)	NOROT	FUMROT
Experimental	12.2	13.4
Calculations	11.2	13.9
Motions	pure rotation "pirouetting"	"pirouetting" AND "scissoring"

SHG and Order

Thin films with axial symmetry: ∞mm

$$\chi^{(2)}_{ZZZ}(-2\omega;\omega,\omega) = NF\beta_{eff}(-2\omega;\omega,\omega) < \cos^3\Theta >$$

$$\chi^{(2)}_{XXZ}(-2\omega;\omega,\omega) = \frac{1}{2}NF\beta_{eff}(-2\omega;\omega,\omega) < \sin^2\Theta\cos\Theta >$$

$$< \cos^3\theta > \propto \left(\frac{1}{5} + \frac{4}{7} < P_2 > + \frac{8}{35} < P_4 >\right)$$

$$< \sin^2\theta\cos\theta > \propto \left(\frac{1}{15} + \frac{1}{21} < P_2 > - \frac{8}{70} < P_4 >\right)$$

ÉCOLE NORMALE SUPÉRIEURE DE LYON

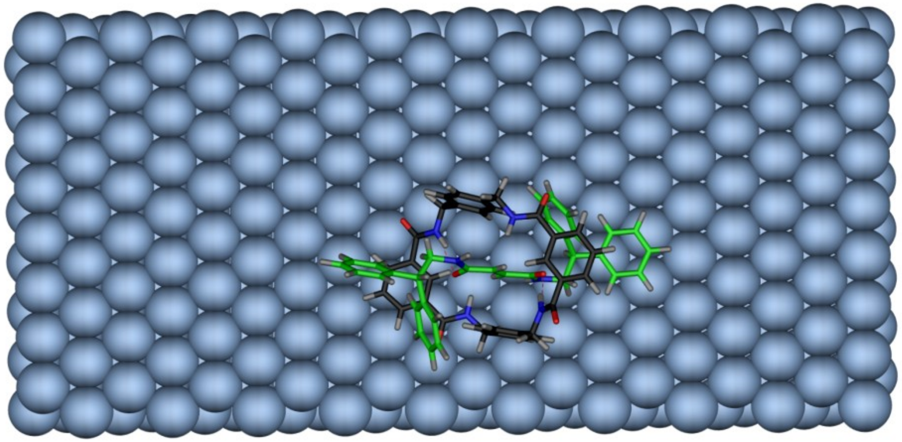
Goals

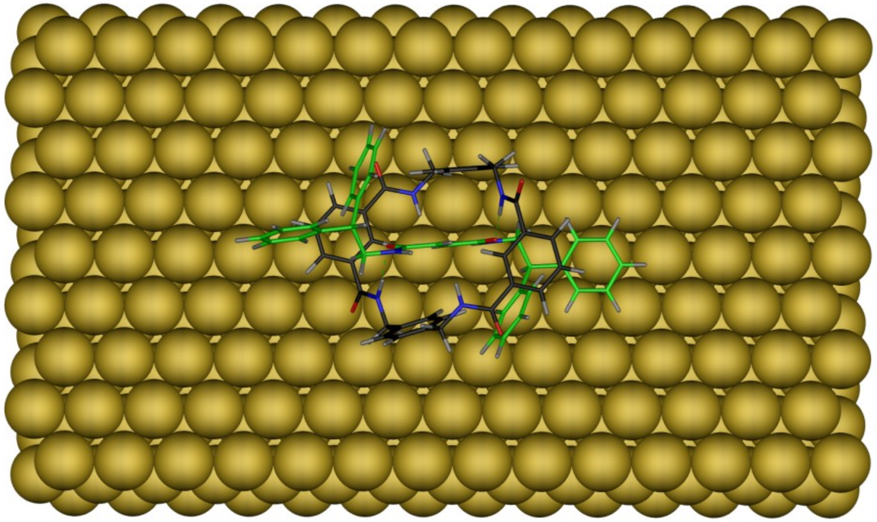
- Test order of molecules in deposited thin layer
- Principle: order determined by the ratio:

$$a = \frac{\chi^{(2)}_{ZZZ}(-2\omega;\omega,\omega)}{\chi^{(2)}_{XXZ}(-2\omega;\omega,\omega)}$$

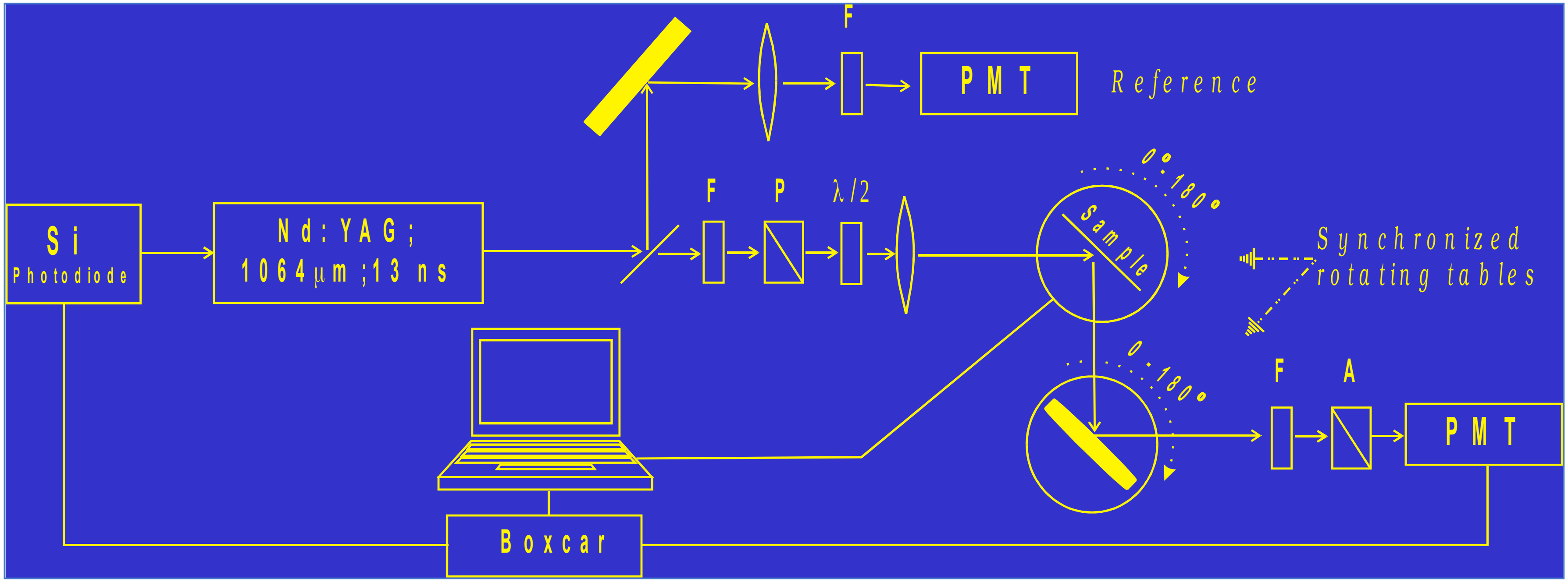
$$1 < a < \infty$$

Fumrot on Ag

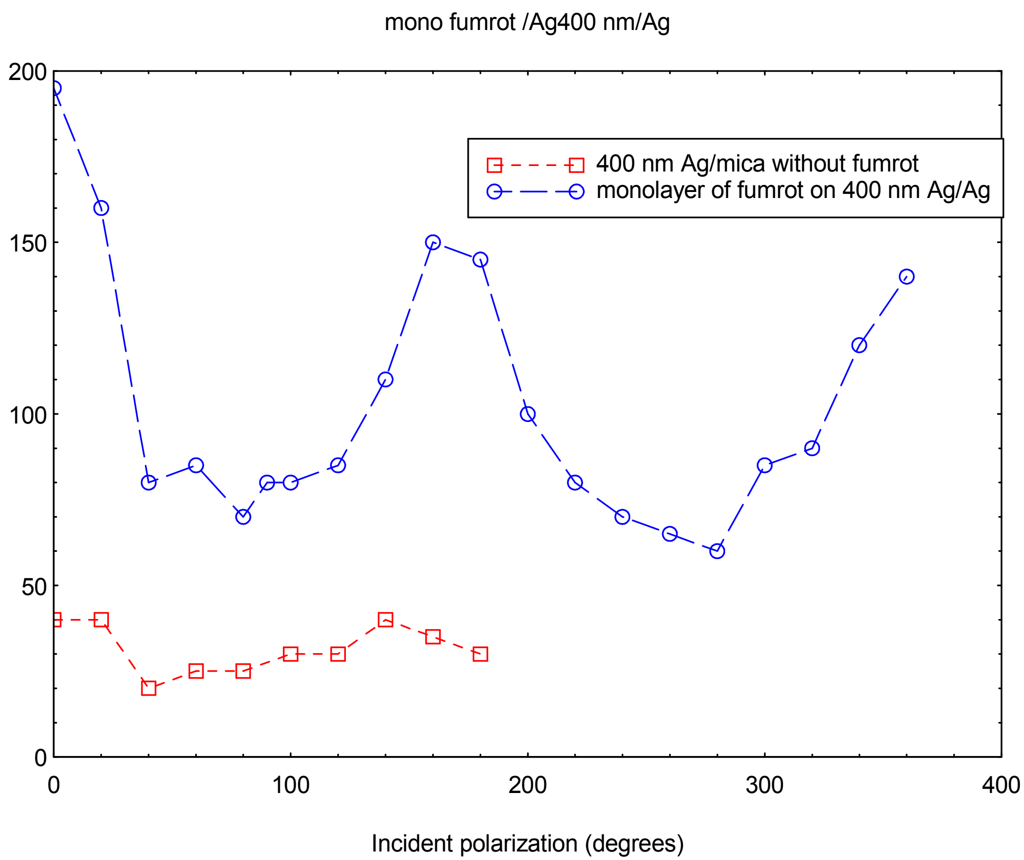




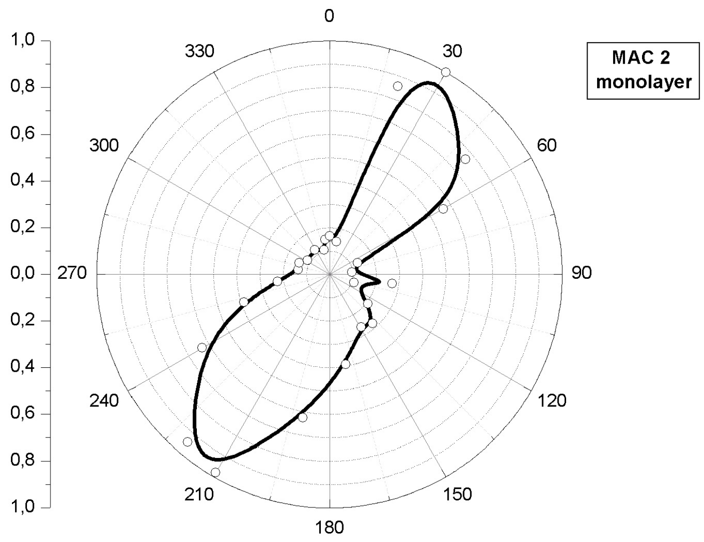
Second Harmonic Generation In Reflection



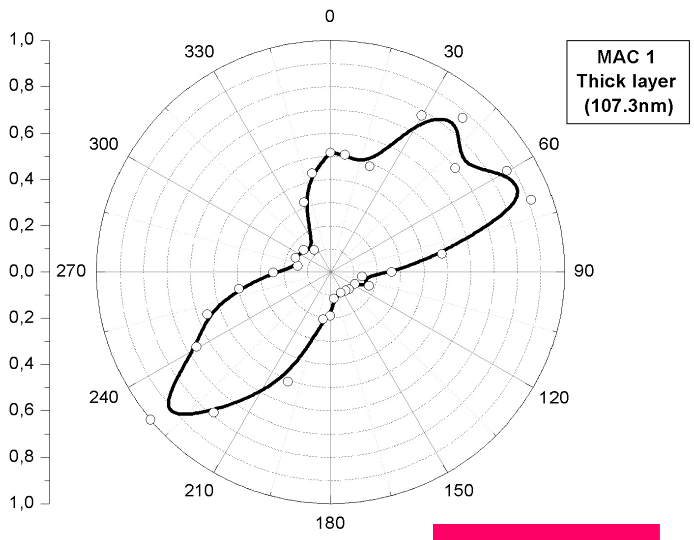
Monolayer of Fumrot



Multi- and monolayer of MAC

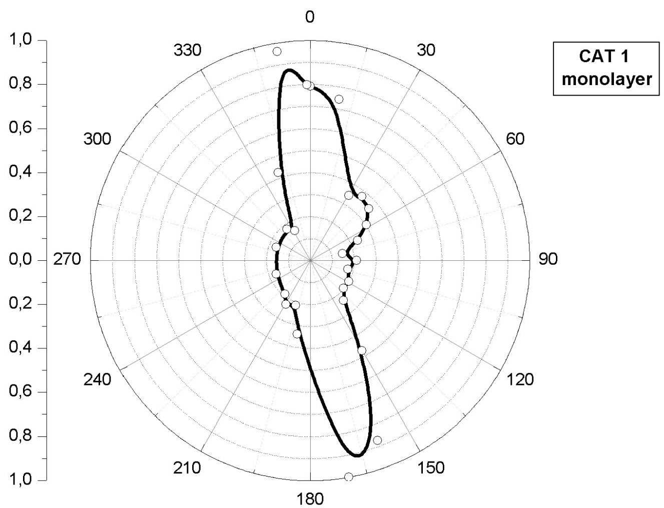


a ≈ 7.2

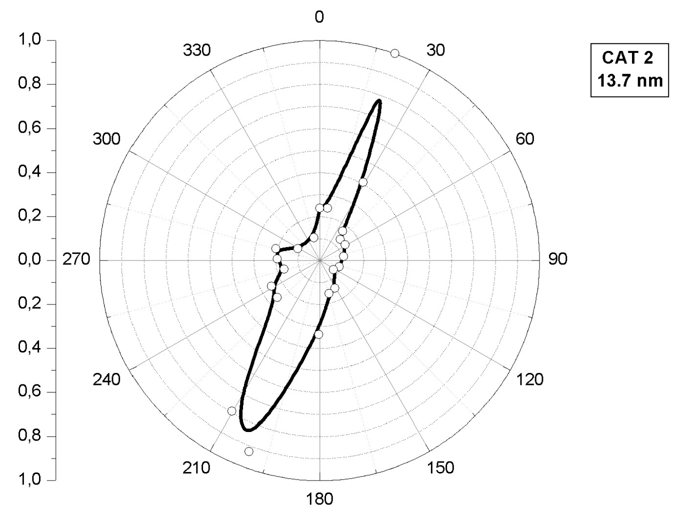


a ≈ 6.6

Monolayer and multilayer of CAT1

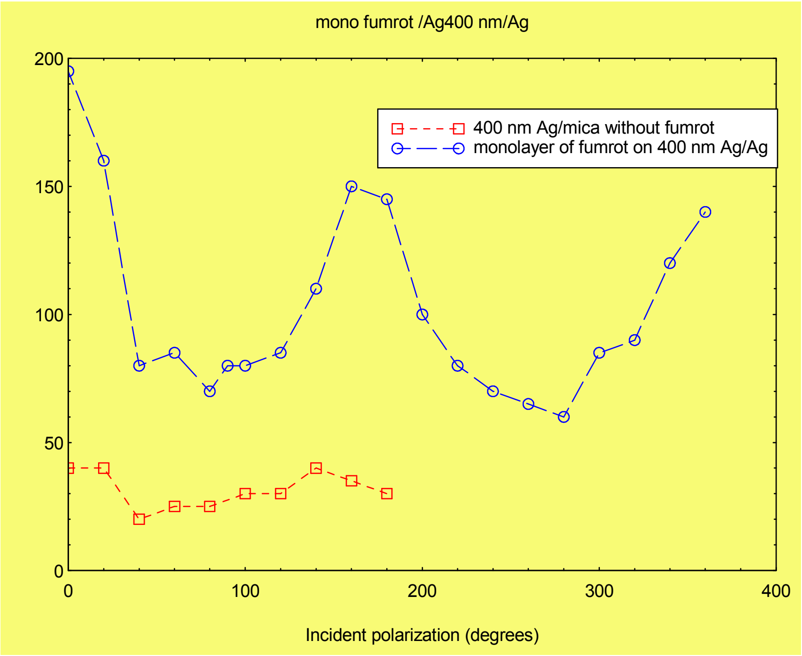


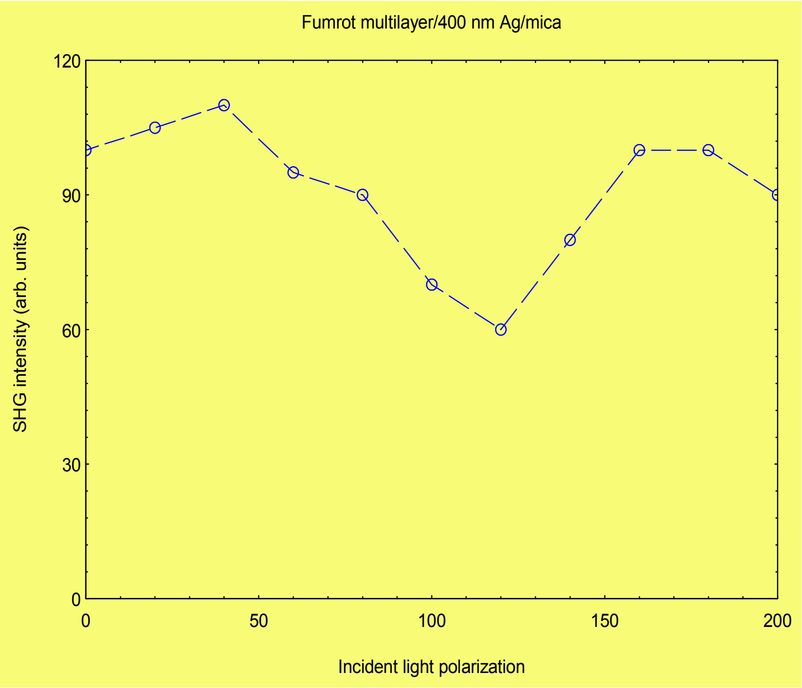
a ≈ 4.8



a ≈ 5.5

Mono- & multilayer of Fumrot





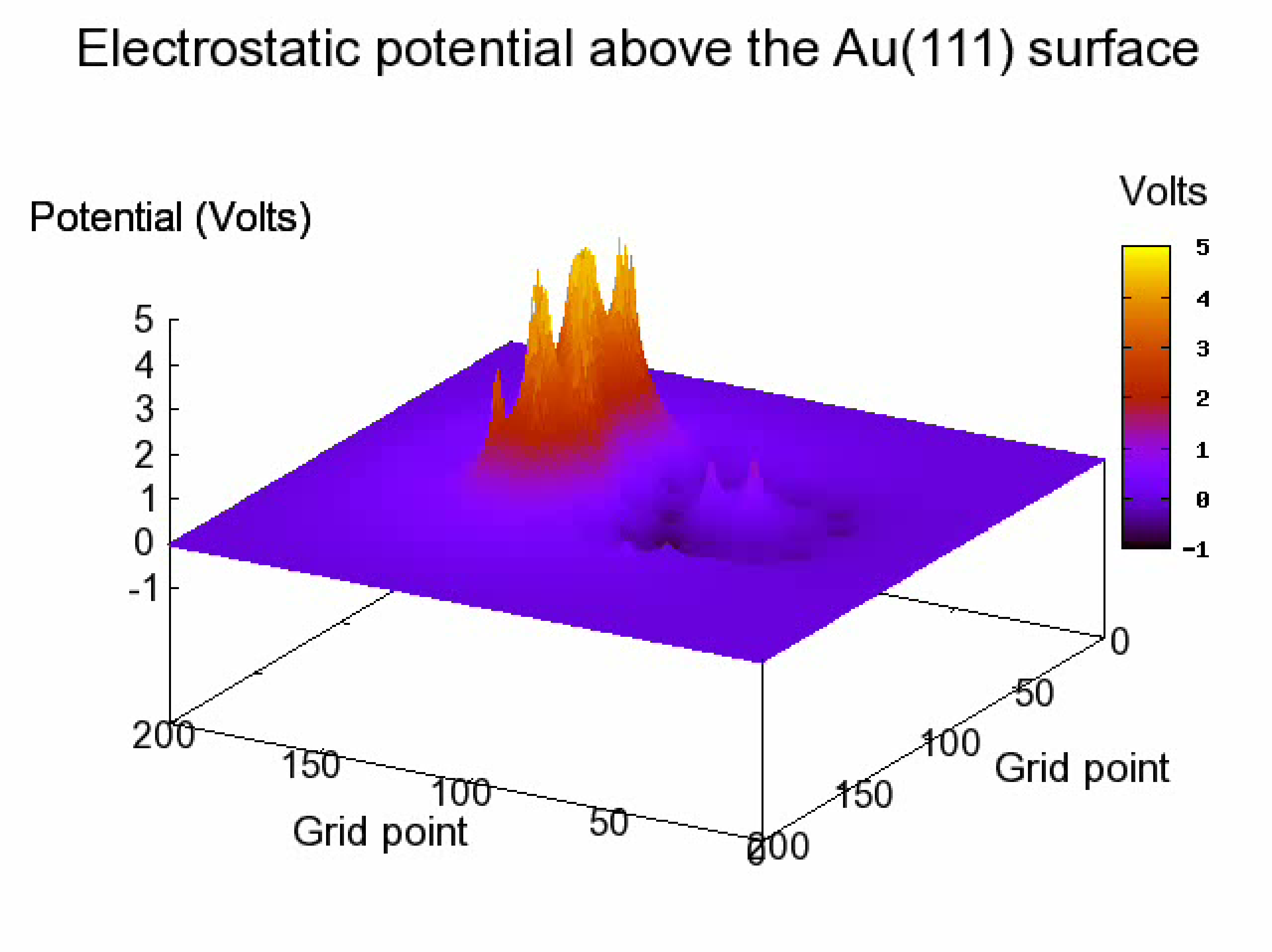
a ≈ 3

a ≈ 1.3

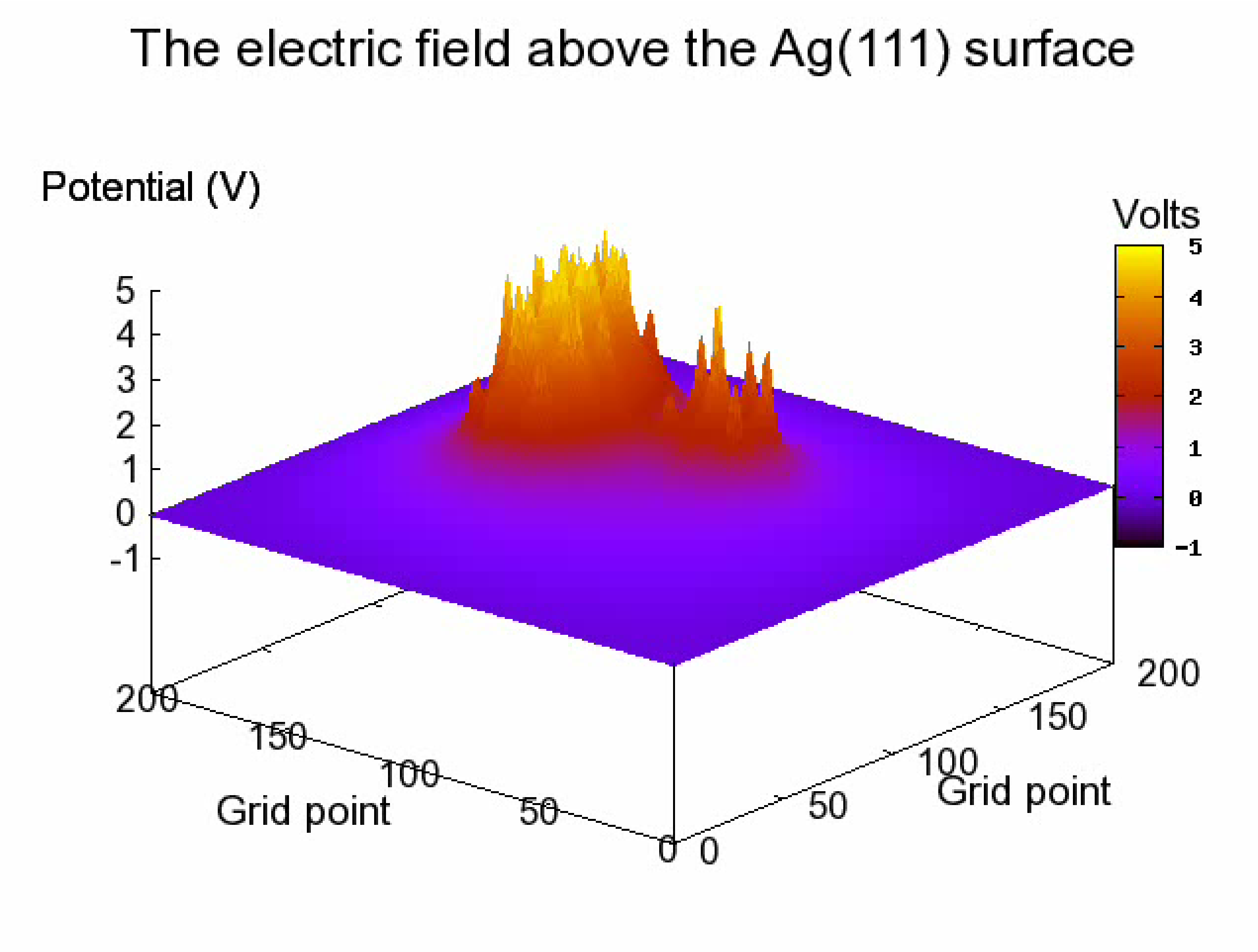
Results

Thin Film	Structure	a
Macrocycle	Multilayer	6.6
Macrocycle	Monolayer	7.2
Catenane	Multilayer	5.5
Catenane	Monolayer	4.8
Fumrot	Multilayer	1.3
Fumrot	Monolayer	3.0

E above Au surface



E above Ag surface



Results of Delphi4 calculations

Rotaxane volume on Au(111): 1372.54 Å^3 in 171 567 grid points

Rotaxane volume on Ag(111): 1340.86 Å^3 in 167 607 grid points

Electric field experienced by the rotaxane on Au(111): 7.0 MV/cm

Electric field experienced by the rotaxane on Ag(111): 15.0 MV/cm

Depth ≈ 9 Å

$\chi^{(2)}$ susceptibility

$$\chi^2(-2\omega;\omega,\omega) = NF\gamma(-2\omega;\omega,\omega,0)E$$

assuming: $\gamma\ (-2\omega;\omega,\omega,0) \approx \gamma\ (-3\omega;\omega,\omega,\omega)$

$$\chi^{(2)EFISH}(-2\omega;\omega,\omega) \approx 24.2\ \text{pm/V}$$

$$\chi^{(2)}_{exper}(-2\omega;\omega,\omega) \approx 23.4\ \text{pm/V}\ (9\text{Å})$$

APPLICATIONS

Electronically Configurable Logic Gates.

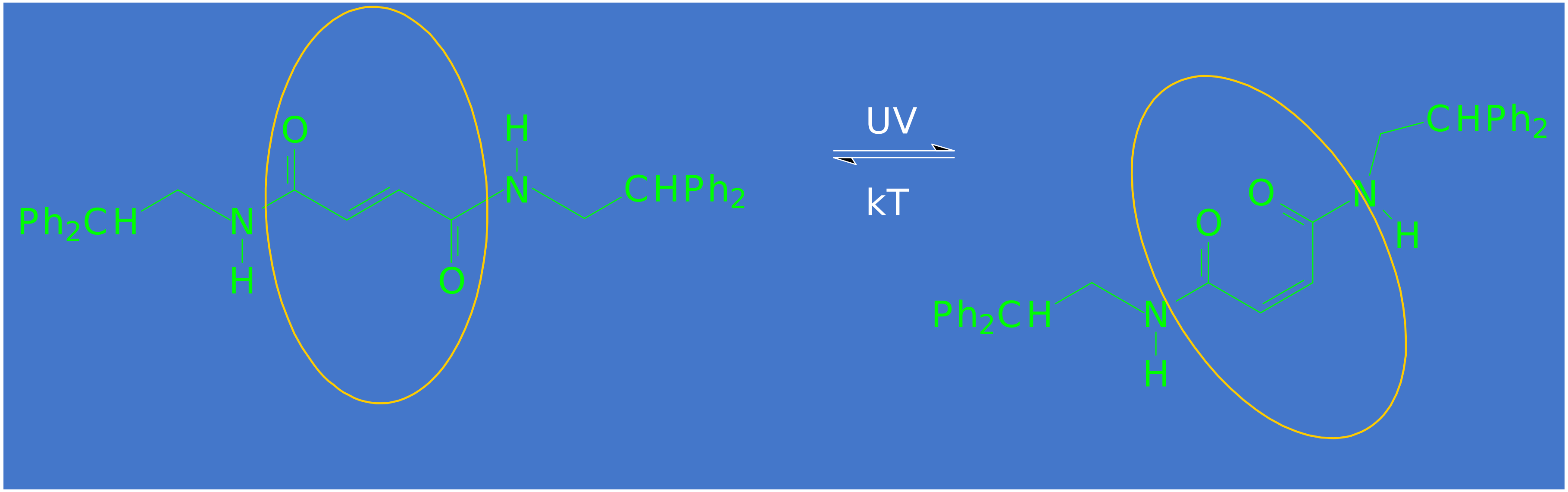
(C. P. Collier et al. Science 285, 391 (1999)

Photoinduced electron transfer coupled to Molecular motion.

(Maria-Jesus Blanco et al. Chem Soc. Rev. 28, 293 (1999)

………………

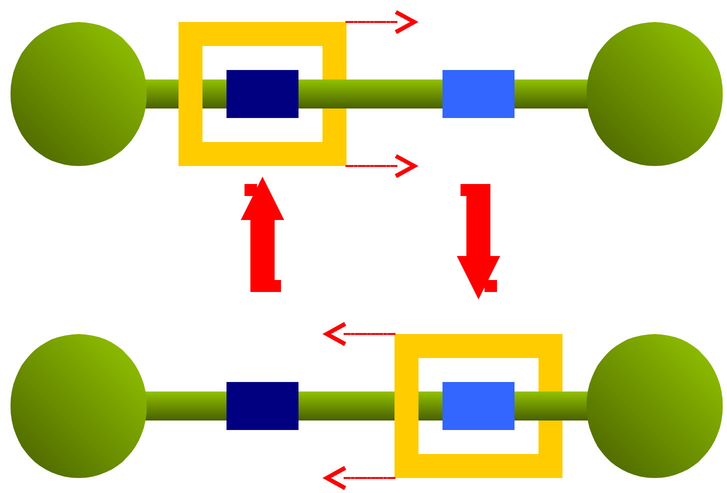
Possible clipping mechanism



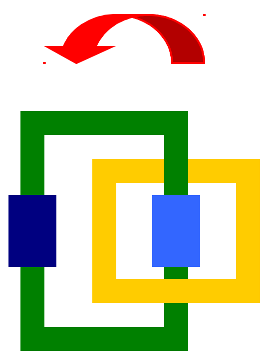
ÉCOLE NORMALE SUPÉRIEURE DE LYON

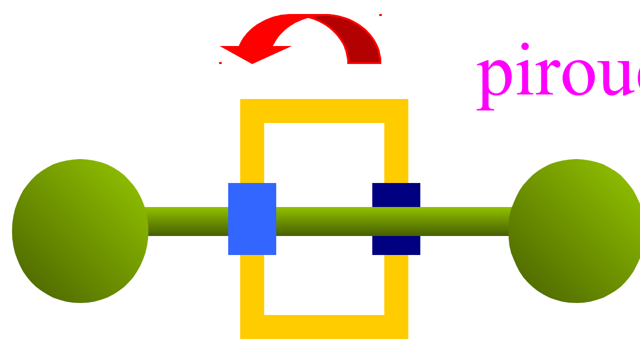
Rotaxanes

shuttling



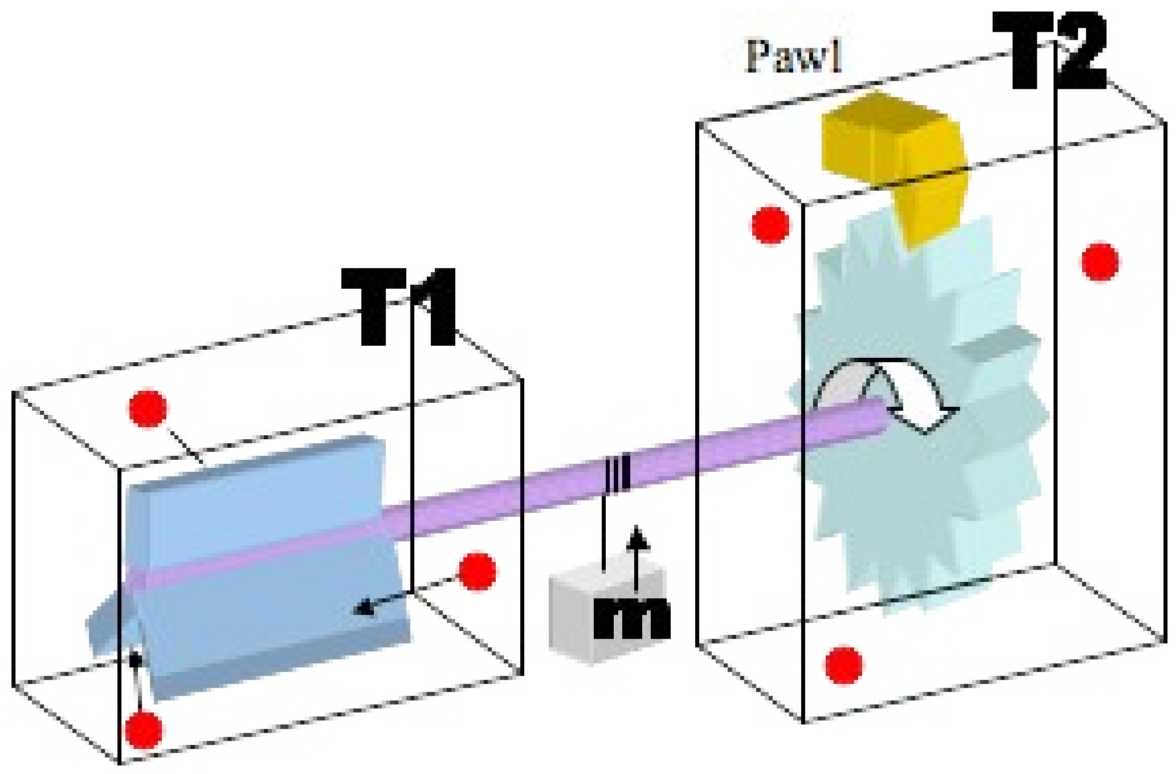
clipping





pirouetting

Brownian ratchet (Smoluchowski)



Heavy atom removal

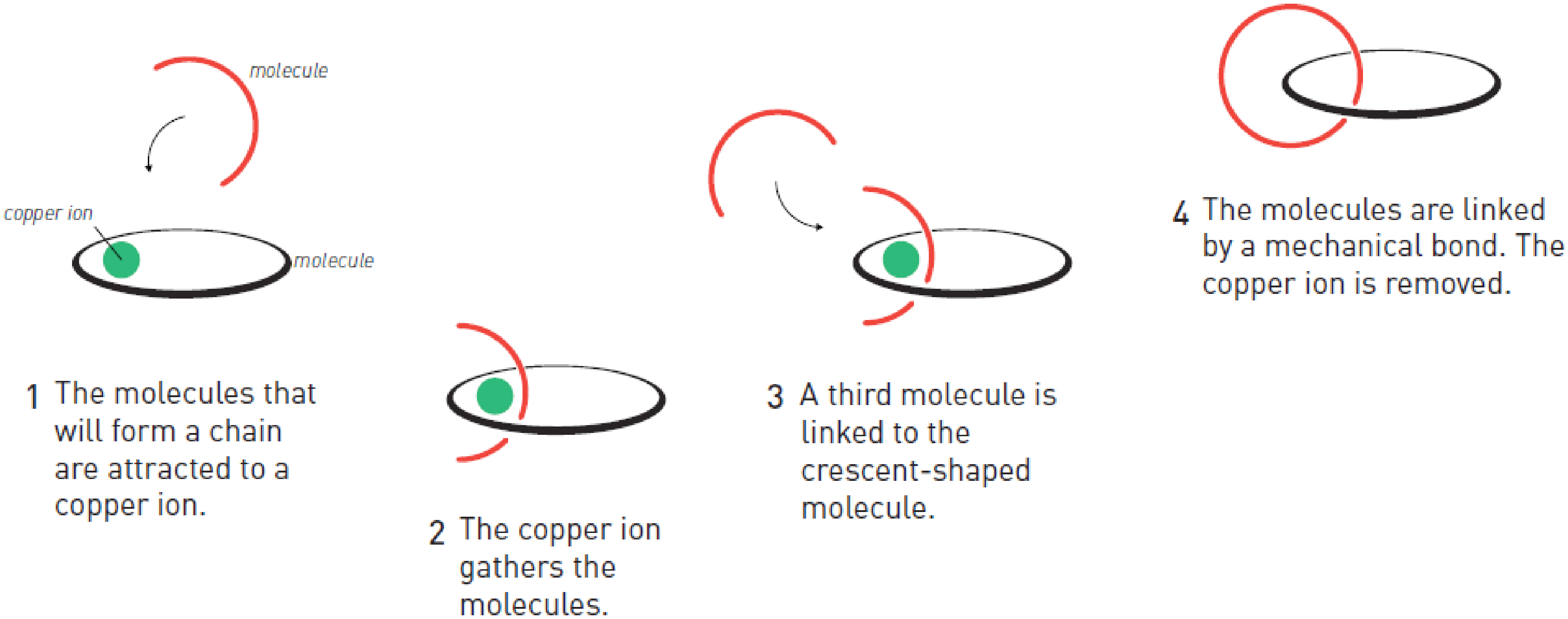


Illustration: ©Johan Jarnestad/The Royal Swedish Academy of Sciences

Summary

- Molecular engineering allows to conceive and synthesize molecules with desired properties
- Control of macroscopic properties through the molecule design
- EO Kerr effect gives information about the macrocycle rotation in Rotaxanes
- Macrocycle rotates slightly faster in NOROT than in FUMROT. The first resonance is ascribed to the macrocycle pirouetting and the second, to the scissoring motion
- The rotation speed can be controlled by the external field
- Use silver plates and cutlry. Gold are OK too
- Applications to come

Dzieki za uwage