Ecole d'ingénieurs et d'architectes de Fribourg
Hochschule für Technik und Architektur Freiburg

Olimpia Mamula Steiner

A. Sinteza diastereoselectiva de nanostructuri chirale auto-asamblate

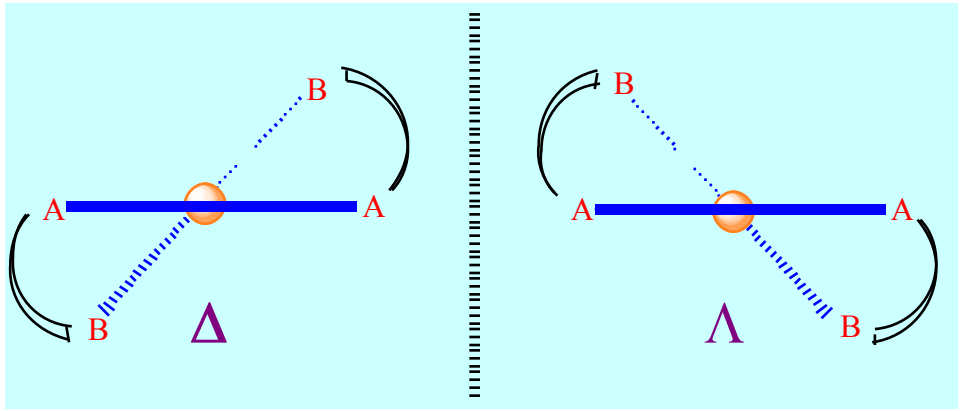
B. Chimie @ EIA Fribourg

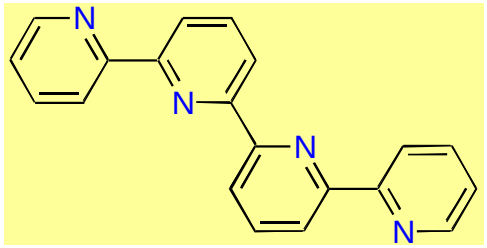
Hes·so FRIBOURG FREIBURG
Haute Ecole Spécialisée de Suisse occidentale
Fachhochschule Westschweiz

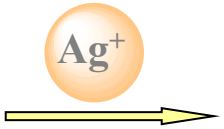
Introducere

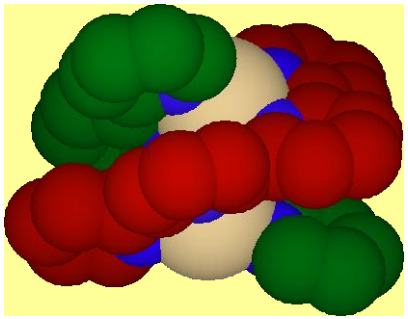
Chiralitate helicoidala in complecsii metalici

Geometrie T-4 / OC-6: liganzi bidentati -→ centru metalic chiral (Λ, Δ)

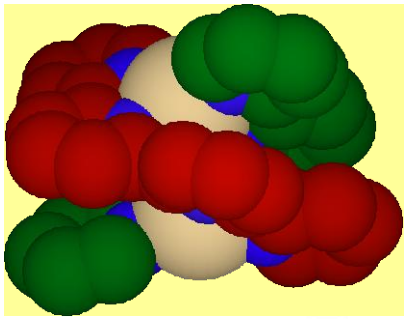








+



ligand tetradentat

P racemat M

Predeterminare chirala

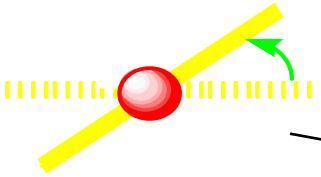
Stereoizomerii: o problema (amestecuri complicate, greu de analizat)

Necesitatea de a controla chiralitatea centrilor metalici

Ligand → **Metal ion** → **Helicate**

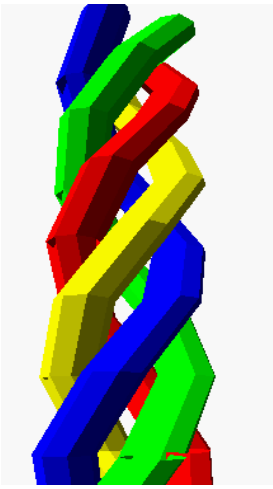
R, S

Coordination



Λ (Δ)

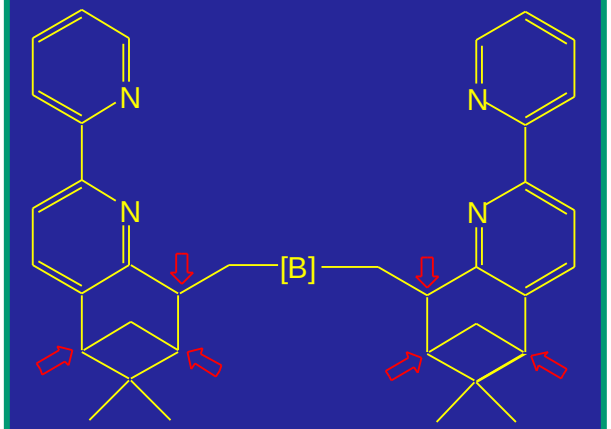
Self-assembly



P (M)

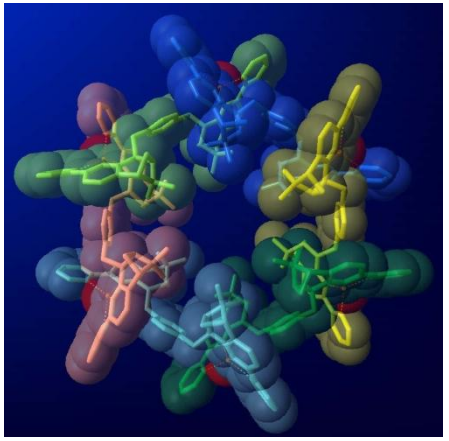
Predeterminare chirala

Pinene bipy Ligands

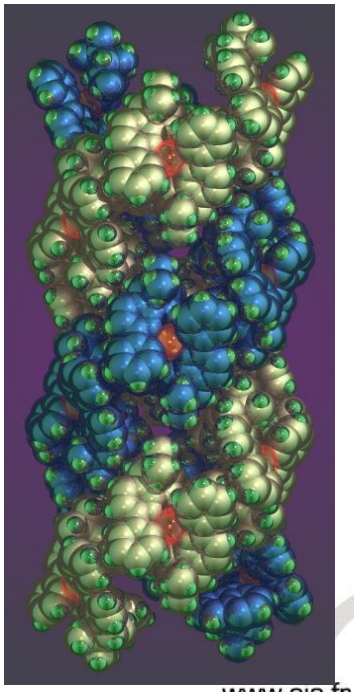


+ metale d

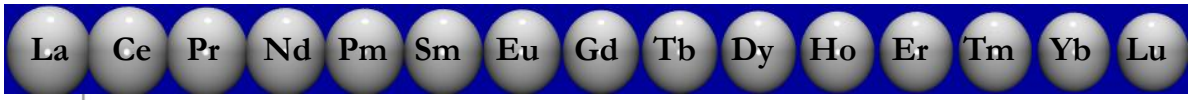
Helicat circular



Polimer tip helix

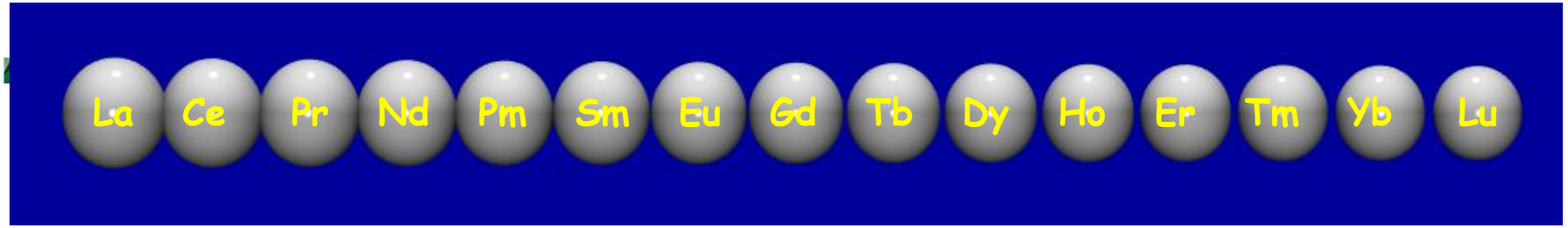


Si lanthanidele (metale 4f)?



Angew. Chem. Int. Ed., **1998**, 289 & **1999**, 2945.

Predeterminare chirala



Structura electronica Ln^{III}:

$[Xe]4f^n$

$5s^25p^6$

→ **Orbitale 4f ecranate**

↓

Legatura dativa Ln^{III}-ligand: electrostatica

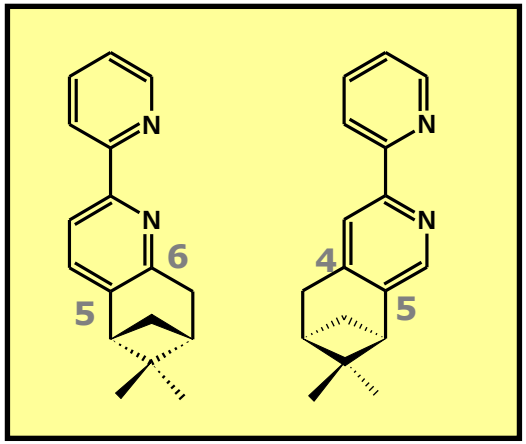
↓

Preferinte sterice minime

(NC variabil, legaturi nedirectionate)

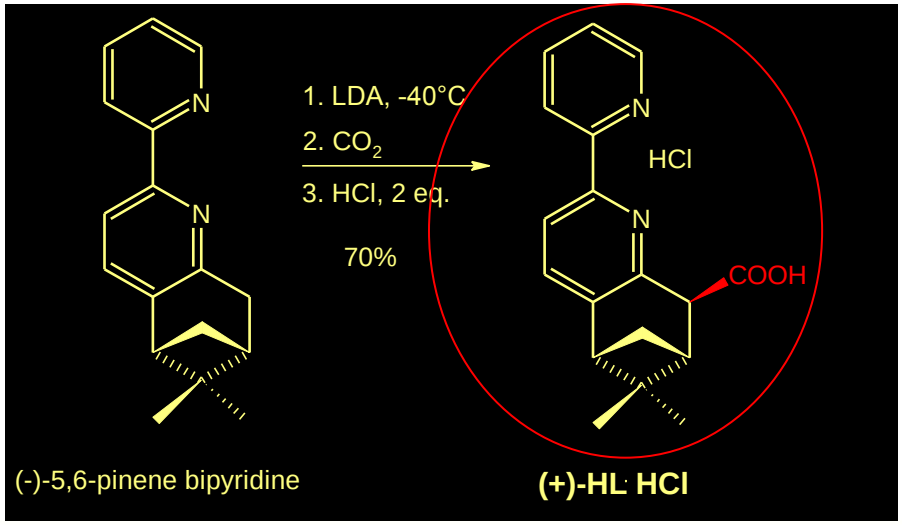
← **Pericol de racemizare**

Predeterminare chirala

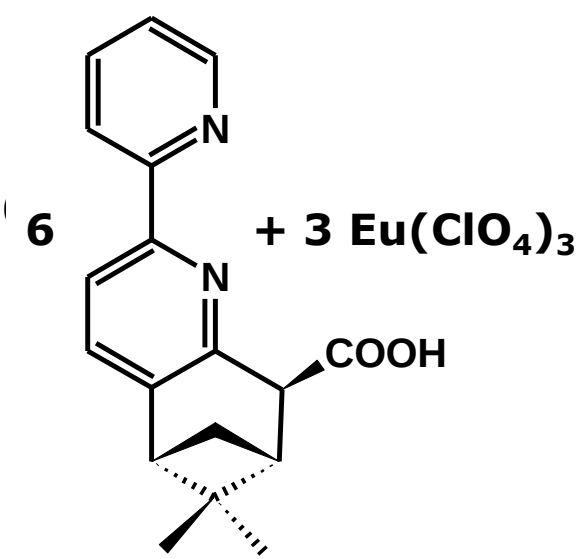


Alegerea liganzilor

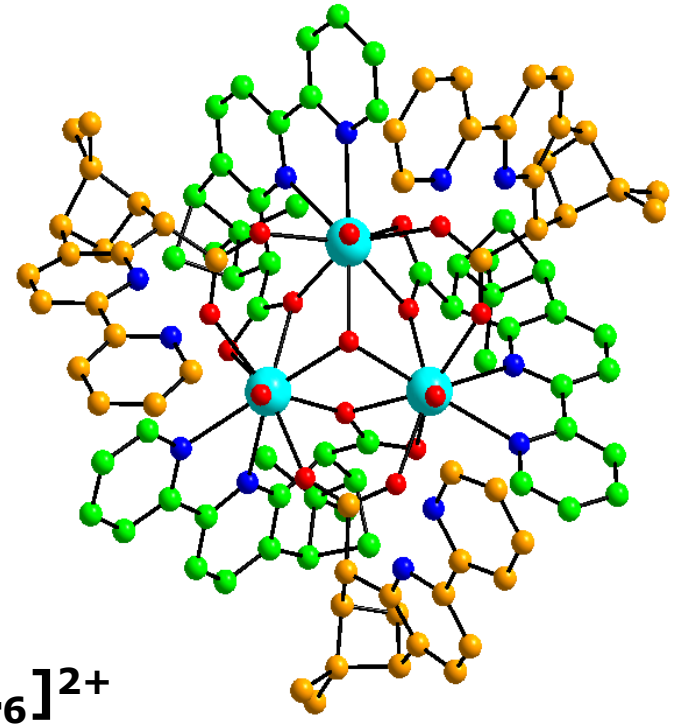
- Enantiopuri (tip 2,2'-pinene-bipyridina)
- Functionalizati cu un grup carboxyl
- Centrii chirali in apropierea siteului de coord.



Nanostructuri chirale auto-asamblate

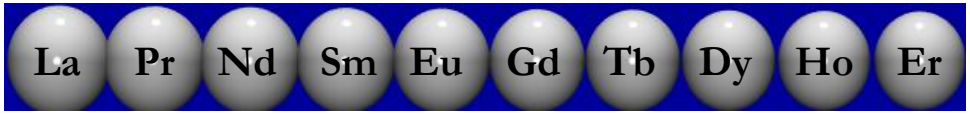


(+)-HL



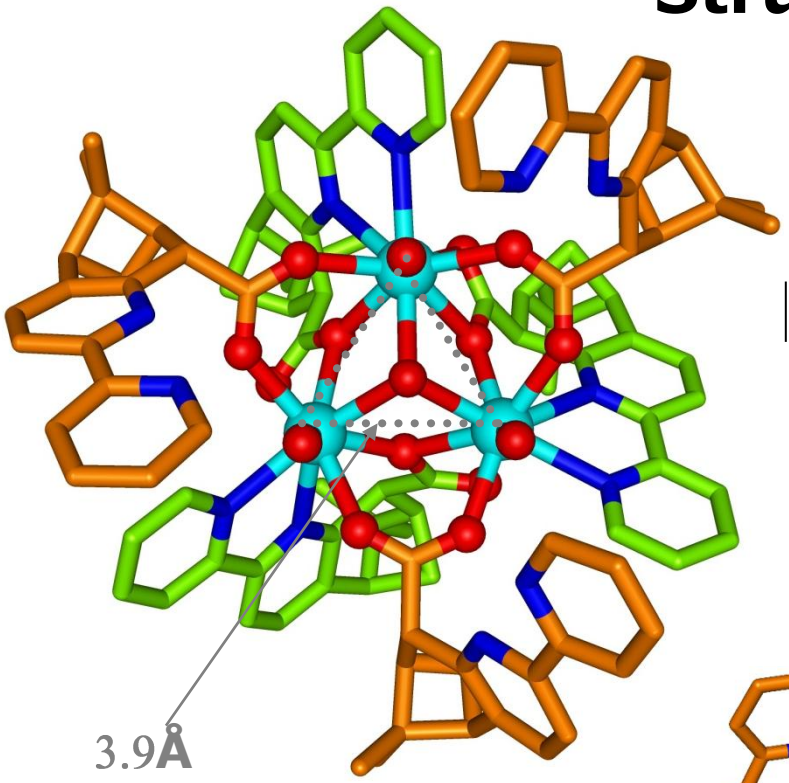
$[Eu_3(\mu^3\text{-}OH)L_6]^{2+}$

Compusi isostructurali obtinuti cu Ln(III):

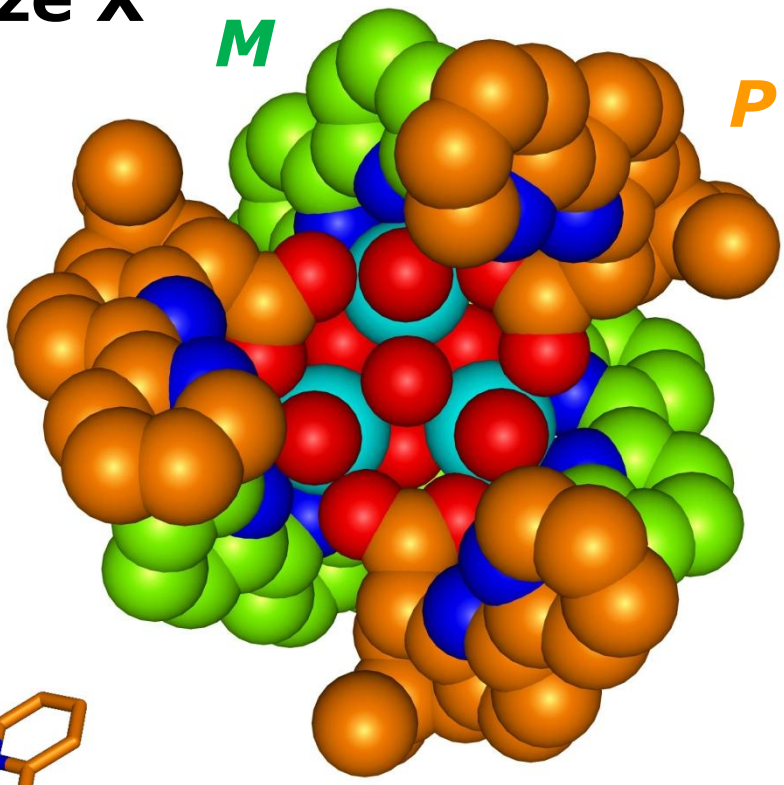


Angew. Chem. Int. Ed., 2005, *44*, 2527

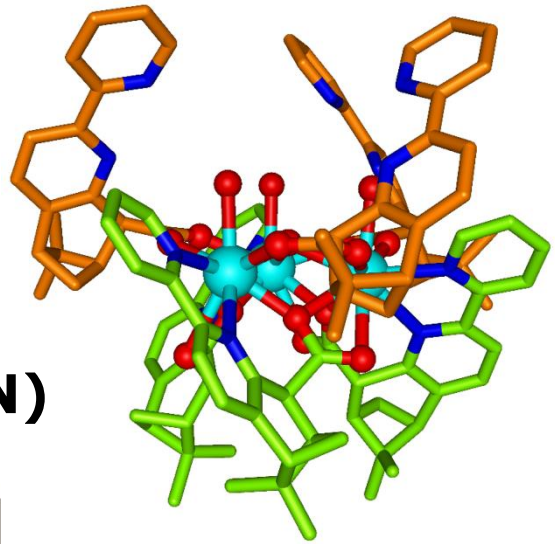
Structuri raze X



|| to C_3 axis



⊥ C_3

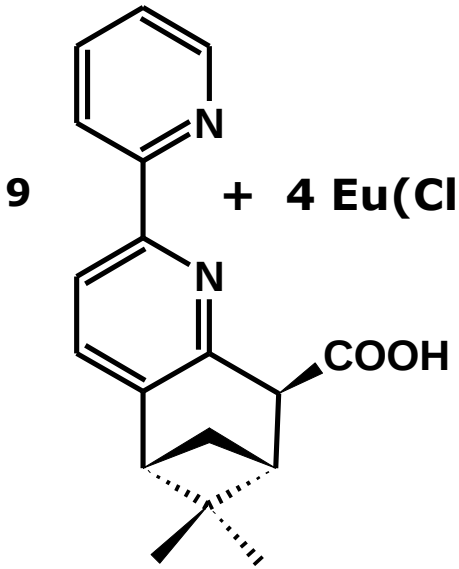


- Dublu helix: *P*, *M*

Doua seturi liganzi:

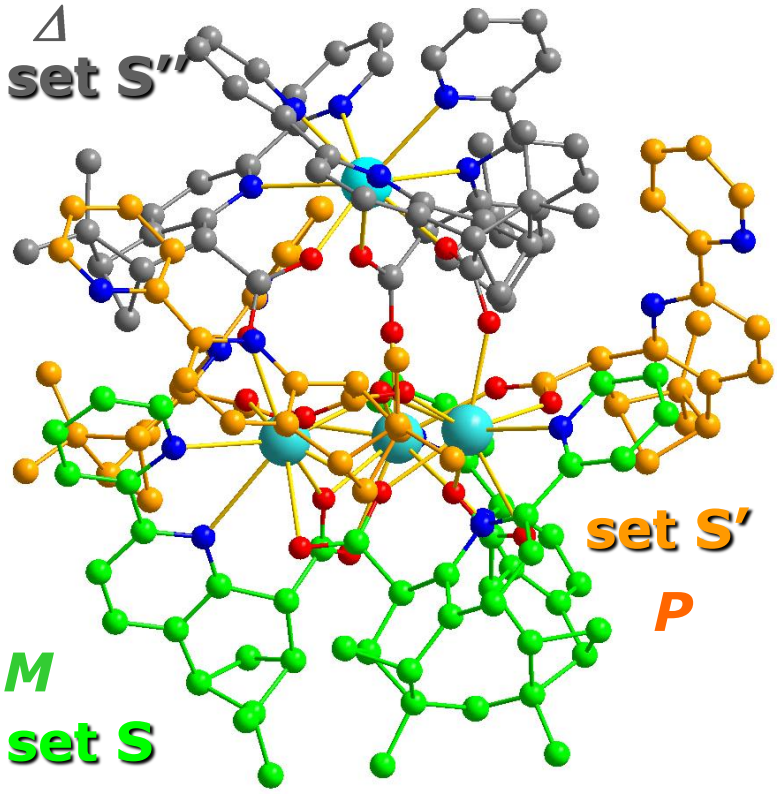
- 3 didentati (OO)
- 3 tetradentati (OONN)

Nanostructuri chirale auto-asamblate



9 + 4 $Eu(ClO_4)_3$ $\xrightarrow[\text{base}]{CH_3CN}$

(+)-HL



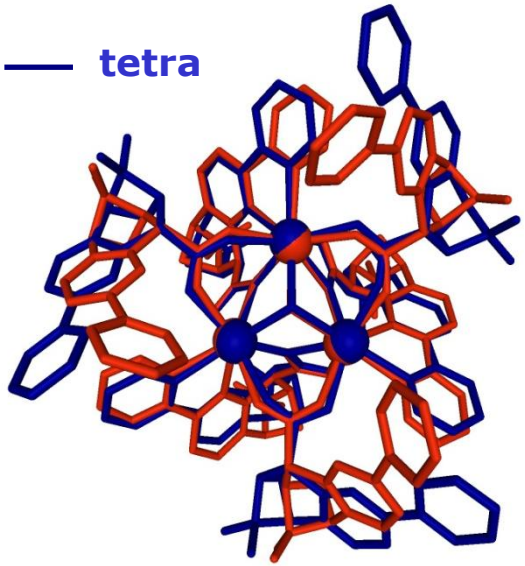
Compusi isostructurali obtinuti cu Ln(III):

Nanostructuri chirale autoasamblate

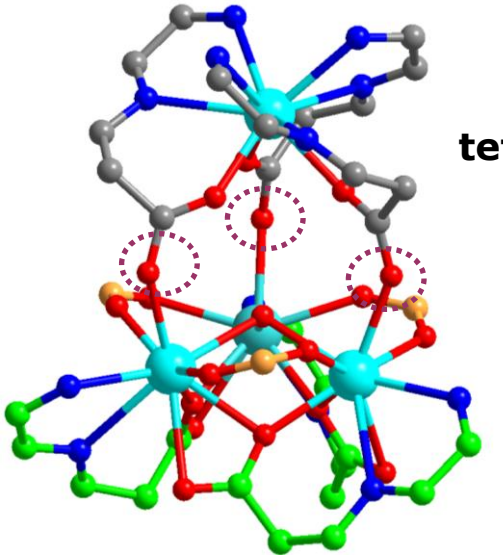
Comparatie structuri tri- si tetranucleare

— **tris**

— **tetra**



"Miez" trinuclear similar



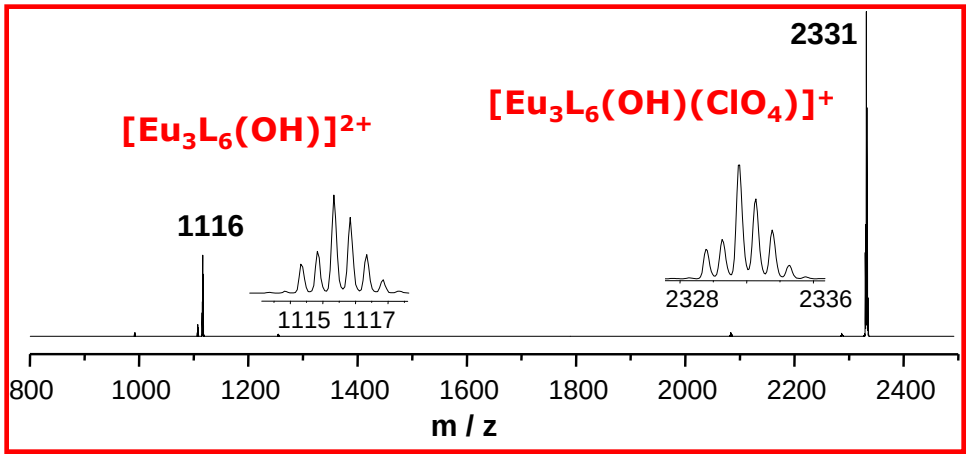
tetra

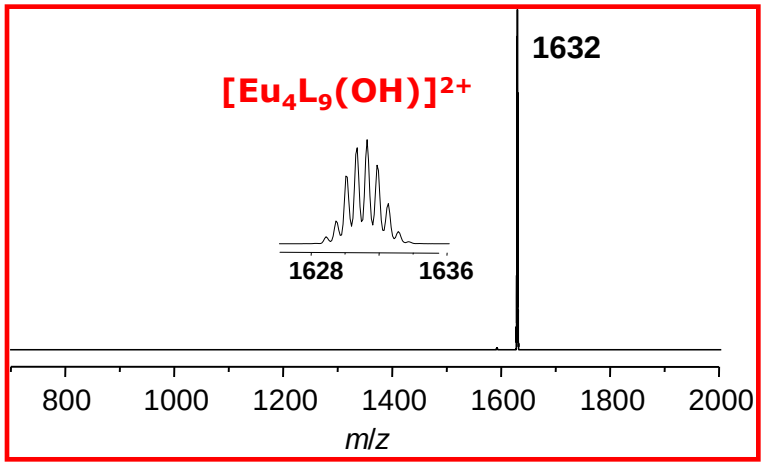
Piramida trigonala:
conexiune prin punti carboxyl

Proprietati

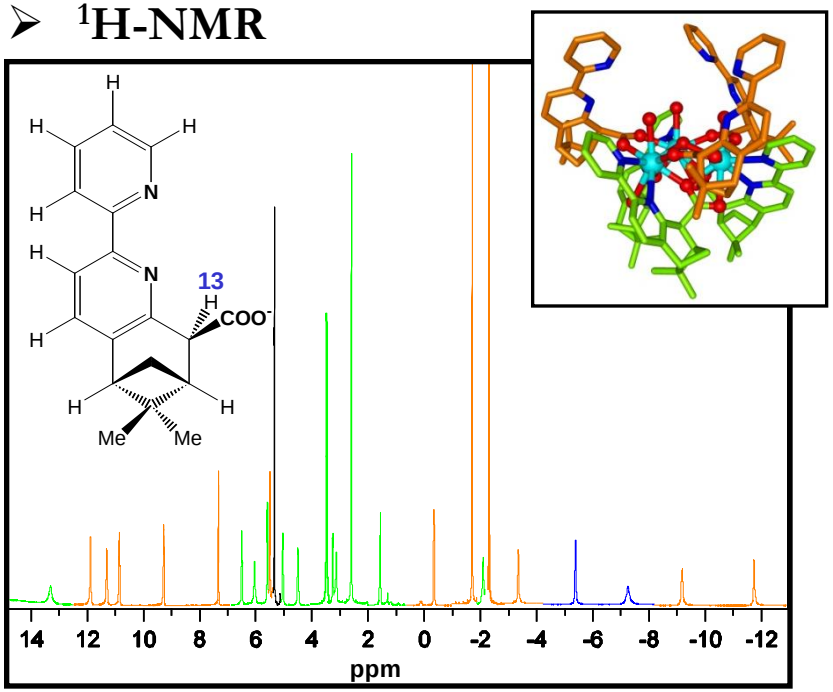
Stabilitate in solutie

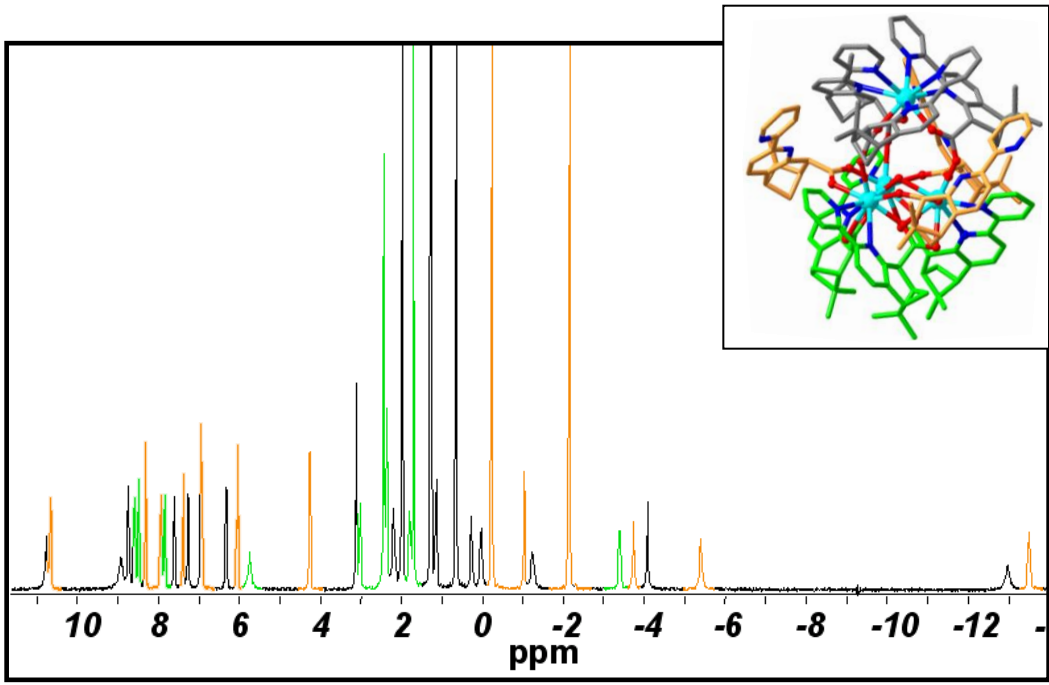
- **ES-MS**





- **^{1}H-NMR**



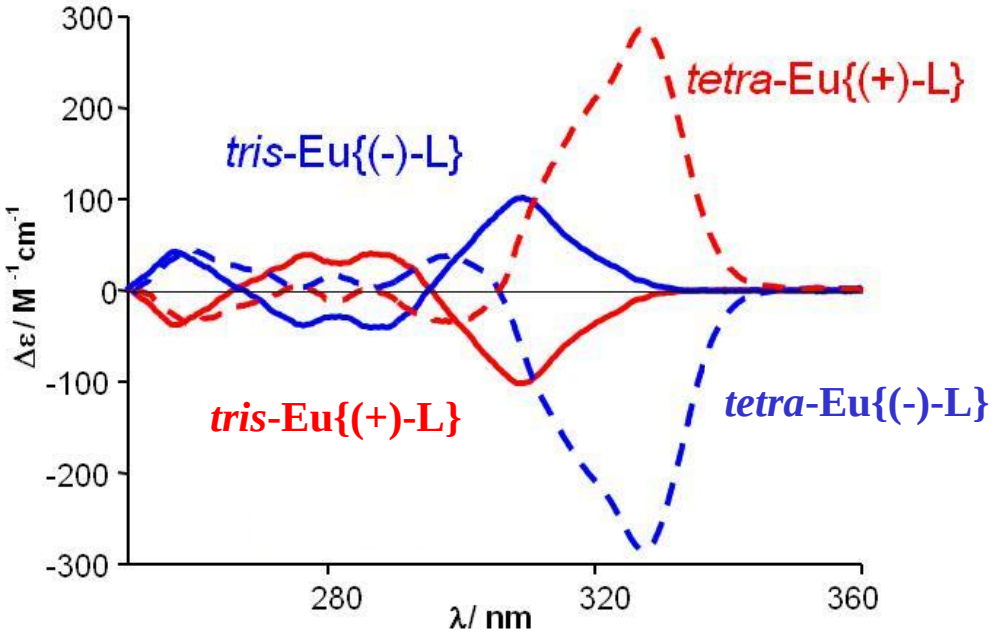


Proprietati

Activitate optica

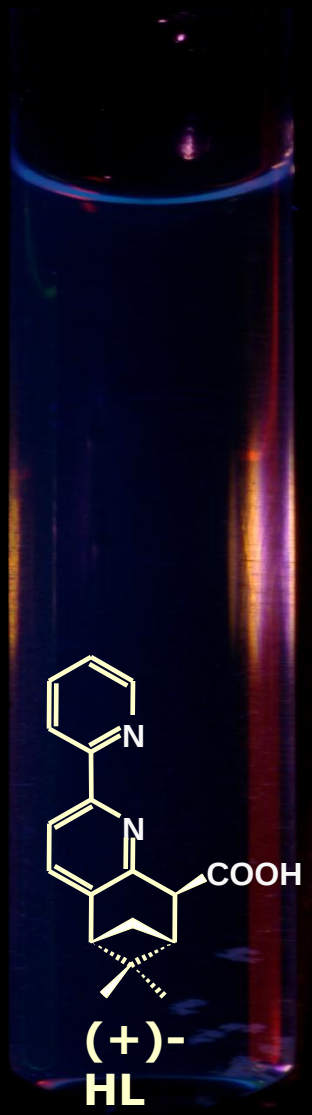
Spectroscopie de Dichroism Circular

- prop. chiroptice in stare fundamentala



- Relatie imagine-imagine in oglinda intre complecsii cu liganzi (+)-L si cei cu liganzi (-)-L
- Benzi mai intense pt tetranuclear (contributia unitatii ML_3)

Luminescenta...

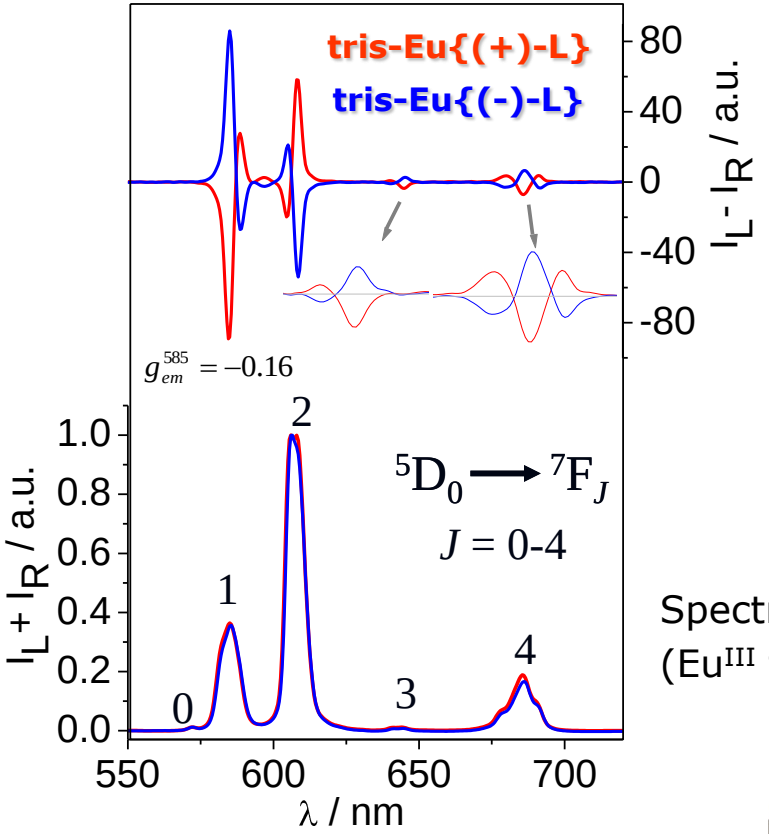


Proprietati

Activitate optica

Spectroscopie de Luminescenta Circular Polarizata (CPL)

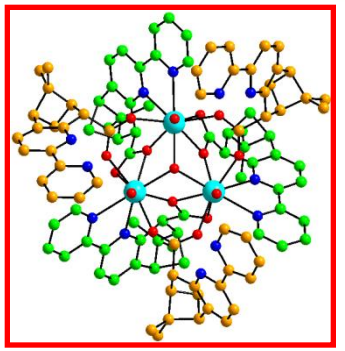
- prop. chiroptice in stare excitata



Relatie imagine-imagine in oglinda

Spectrul total de luminescence (Eu^{III} transitions)

Proprietati



tris

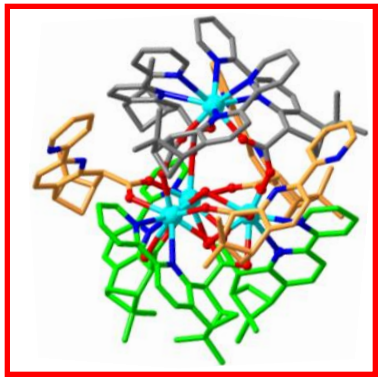
$$6\ (+)\text{-}L^- + 3\ Ln(ClO_4)_3 \cdot x\ H_2O \xrightarrow{MeOH}$$

Switching supramolecular

$+ H_2O$ / $- H_2O$

Solvent: CH_3CN

$$9\ (+)\text{-}L^- + 4\ Ln(ClO_4)_3 \cdot x\ H_2O \xrightarrow{CH_3CN}$$



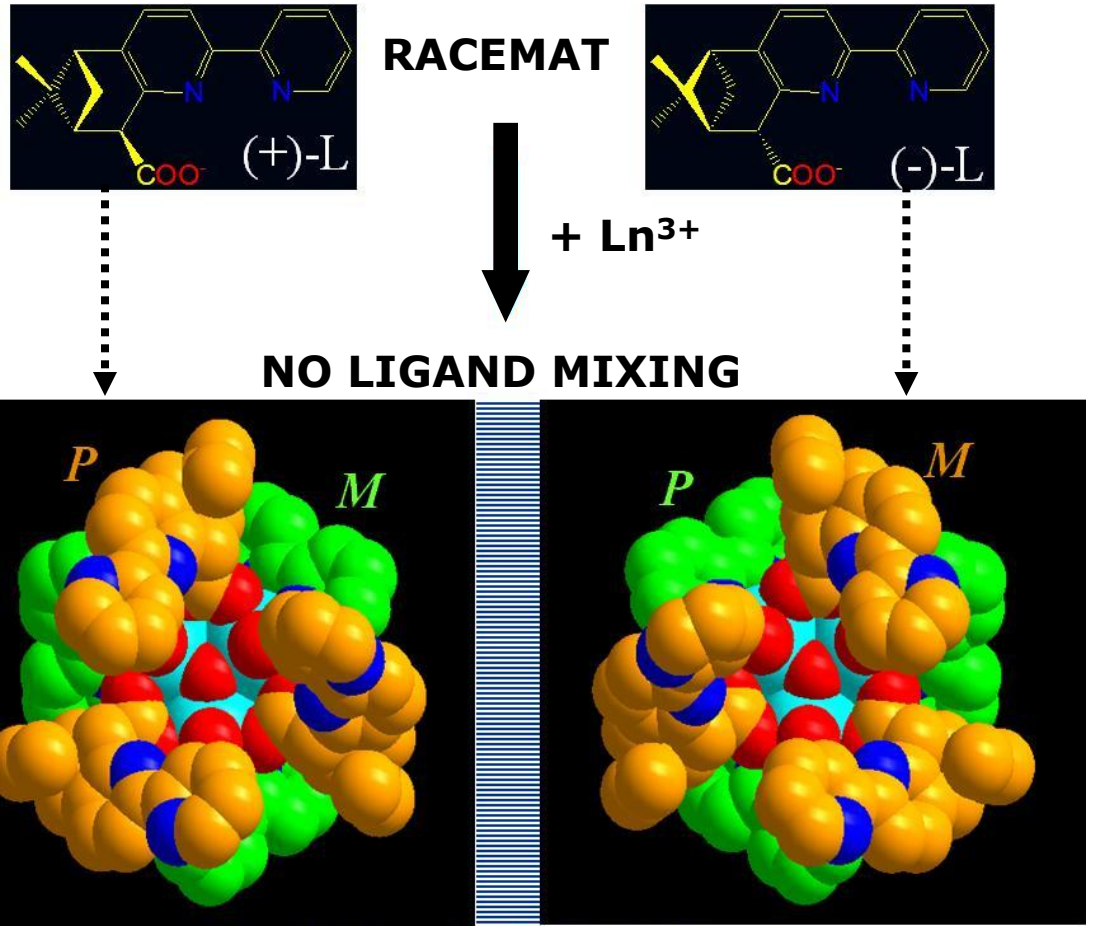
tetra

$$a\ [Ln_3L_6(OH)(H_2O)_3](ClO_4)_2 \rightleftharpoons b\ [Ln_4L_9(OH)](ClO_4)_2 + \{c\ Ln^{3+} + d\ L^- + e\ OH^- + f\ ClO_4^- + 3a\ H_2O\}$$

tris — tetra — **minor species**

Proprietati

Recunoastere Chirala



- **100% in cazul speciilor tris**
- **numai partiala in cazul speciilor tetra**

Concluzii

✓ **Utilizarea liganzilor de tip pinen-bipiridina functionalizati cu un grup carboxyl permite obtinerea de complecsi enantiopuri de lanthanide**

✓ **O noua clasa de nanostructuri enantiopure tri- si tetranucleare auto-asamblate a fost obtinuta prin sinteza diastereoselectiva**

✓ **Interconversia intre speciile tri- si tetranucleare a fost studiata**

✓ **In cazul in care auto-asamblarea se face plecand de la racematul ligandului, recunoasterea chirala poate sa fie totala (racemat final)**

Concluzii

Multumiri

- Marco Lama: PhD student

- Prof. Reiko Kuroda & Prof. Asao Nakamura (Japan): CPL
- Prof. Luisa de Cola (Germany): Photophysics

- Prof. H. Stoeckli-Evans (Switzerland)
- Dr. R. Scopelitti (Switzerland)
- Dr. S. Shova (Moldavia)

} X-ray

- Swiss National Science Foundation
- EPFL

Ecole d'ingénieurs et d'architectes de Fribourg
Hochschule für Technik und Architektur Freiburg

Olimpia Mamula Steiner

Chimie @ EIA

(Universitatea de Stiinte Aplicate din vestul Elvetiei)

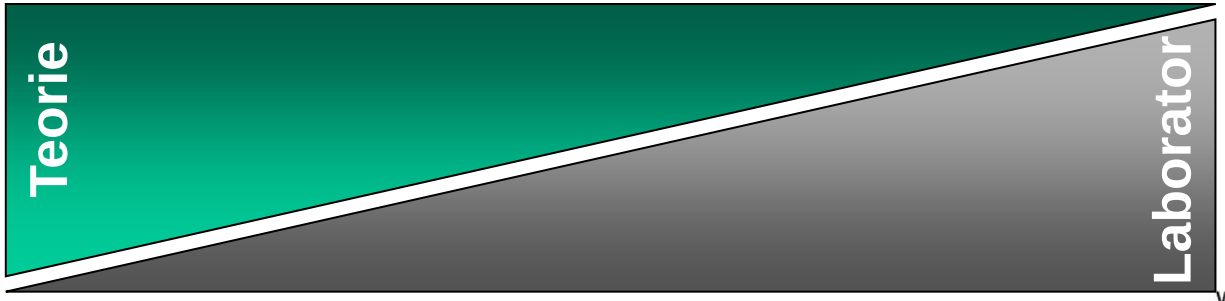
Hes·so FRIBOURG FREIBURG
Haute Ecole Spécialisée de Suisse occidentale
Fachhochschule Westschweiz

Ingineri Chimisti: Bachelor / Master

--→ capabili sa identifice si sa rezolve probleme stiintifice / tehnice in domeniul chimiei aplicate si industriale

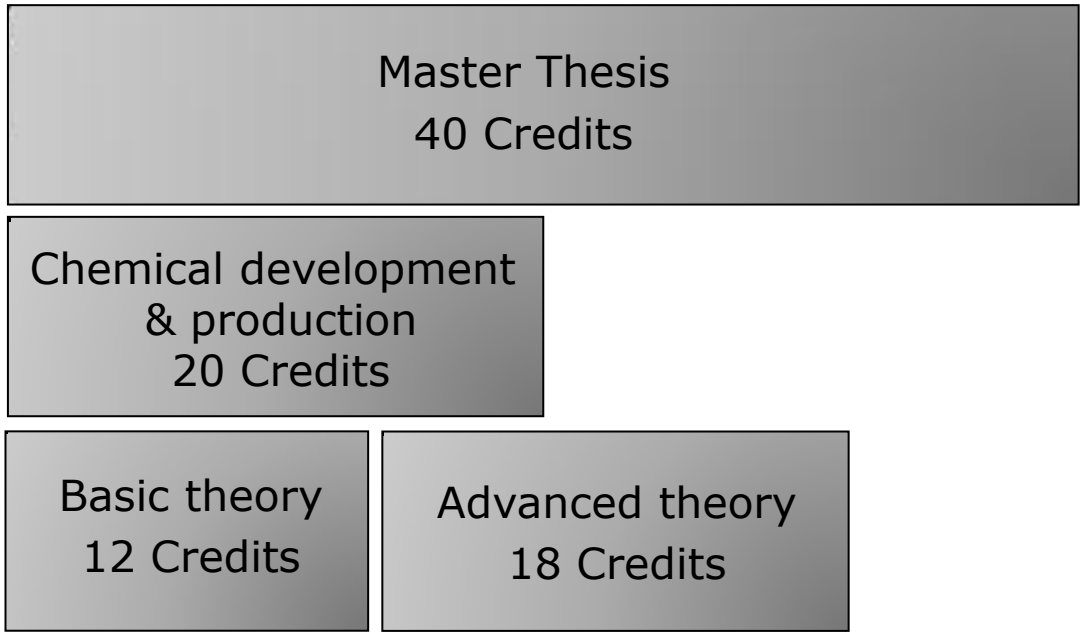
Curriculum Bachelor

An I	An II	An III
Mate & Fizica 1 — 24	Mate & Fizica 2 — 11	Chimie aplicata 2 — 12
Chimie — 21	Chimie aplicata 1 — 21	Chimie industriala 3 — 12
Limbi & Comunicare — 9	Chimie Industriala 1 & 2 — 22	Lucrari practice avansate — 18
Cursuri la alegere — 6	Cursuri la alegere — 6	Proiect semestru — 6
		Proiect Bachelor — 12



Curriculum Master of Science HES-SO

- Orientare: **Chemical Development and Production**”



Activitati R&D: chimie aplicata

➢ Sinteza organica:

- Cataliza chirala
- Reactii de oxidare
- Modificari de sinteze in sens ecologic
- Solventi ecologici
  - -Lichide ionice
- Reactii in sistem continu
  - - Microreactoare

➢ Chimie fizica:

- Termocinetica
  - - Calorimetrie
  - - Spectroscopie optica (IR, Raman)
  - - Chimioluminescenta
- Modificare de suprafete
  - - Electrochimie
- Formulari de produsi finali
  - - Rheologie

➢ Chimie analitica:

- On-line monitoring
  - - IR, UV-Vis, HPLC, GC, MS
- Dezvoltare de sisteme de masura "low-cost"
  - - Electroforeza capilara

depistarea rapida a medicamentelor contrafacute

Activitati R&D: chimie industriala

Optimizarea procedeelor:

- Screening technologies with microreactors including on line analytics (IR, MS)

Automatizare:

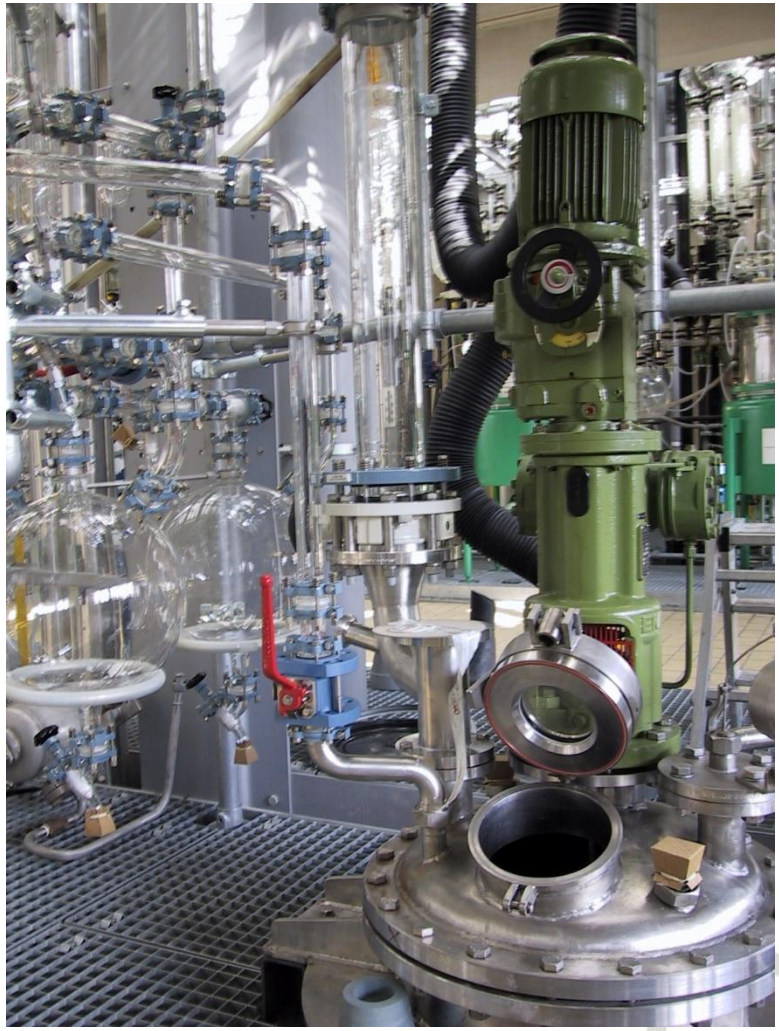
- on-line monitoring with GC on industrial distillation columns
- nanoparticule cu suprafata modificata

Productie:

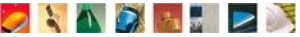
- microparticule
- nanoparticule cu suprafata modificata

Tehnici de separare:

- reciclarea solventilor
- tratament de deseuri in situ



www.eia-fr.ch



« Nu exista drum spre fericire, fericirea e drumul… »

EIA Fibourg : Prof.

Swatch Group R&D (Basel, Neuchatel)

Conducator Doctorat

UNIL + EPFL: Prof. Asist.

Univ. Basel: Postdoctorat — Edwin C. Constable

Univ. Fribourg: Doctorat — Alex von Zelewsky

EPFL: Master in ingineria si managementul mediului

Bursa a Confederatiei obtinuta prin concurs (Ambasada Elvetiei)

Univ. Bucuresti – Chimie anorganica — Maria Brezeanu

...