# *Abstract booklet Journées de l'association CenTRA*

## *June 11th–12th, 2025*

Website: https://felements.fr/journees-de-lassociation-centra/

Edited on June 3, 2025

# Journées de l'association CenTRA

The UCCS (Unité de Catalyse et Chimie du Solide, UMR 8181) and the PhLAM (Physique Lasers Atomes et Molécules, UMR 8523) institutes are pleased to host the Journées de l'association CenTRA from June 11th to June 12th on the Lille campus.

This event series offers an informal and interdisciplinary forum for the discussion of current advances on the physical and chemical properties of lanthanide- and actinide-based molecules, compounds and alloys.

The Organizing and Scientific Committee would like to warmly thank the Chevreul Institute for providing the venue to host this congress, and would like to give special mention to Mr. Christophe Penverne for his invaluable assistance in organizing this event.

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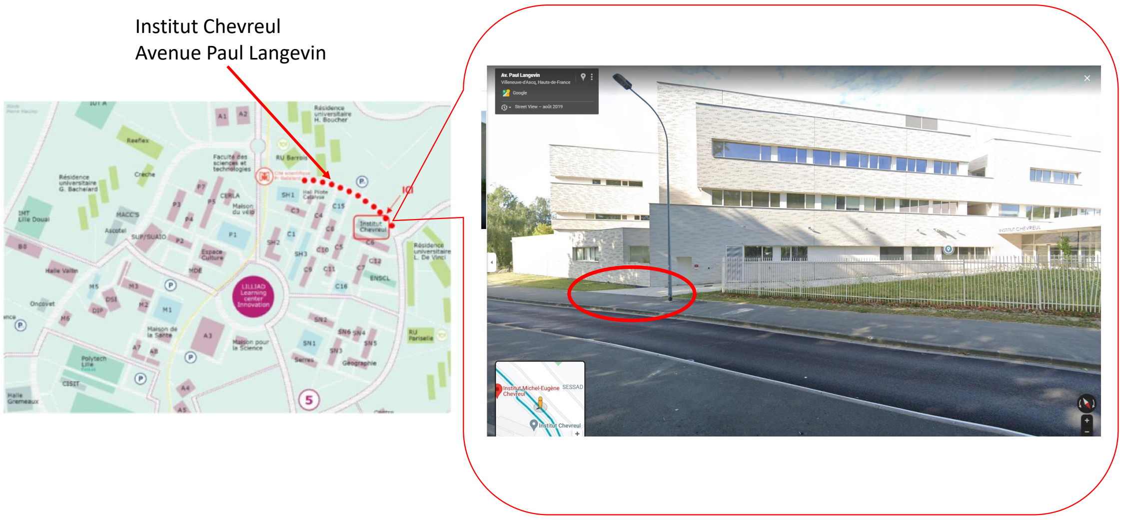
# Conference information

## Conference location

L'Institut Chevreul est facilement accessible depuis le métro, ligne 1, arrêt Cité Scientifique :



Acces à l'institut Chevreul

## Subway access

### From Lille Flandres railway station

- Take subway line 1 toward “4 Cantons-Stade Pierre Mauroy”
- Stop at terminus “Cite Scientifique"
- Exit the subway station to the right and walk 3 minutes to the Institut Chevreuil building

This book contains all abstracts accepted. The contributions are identified by

- PL for Plenary talks

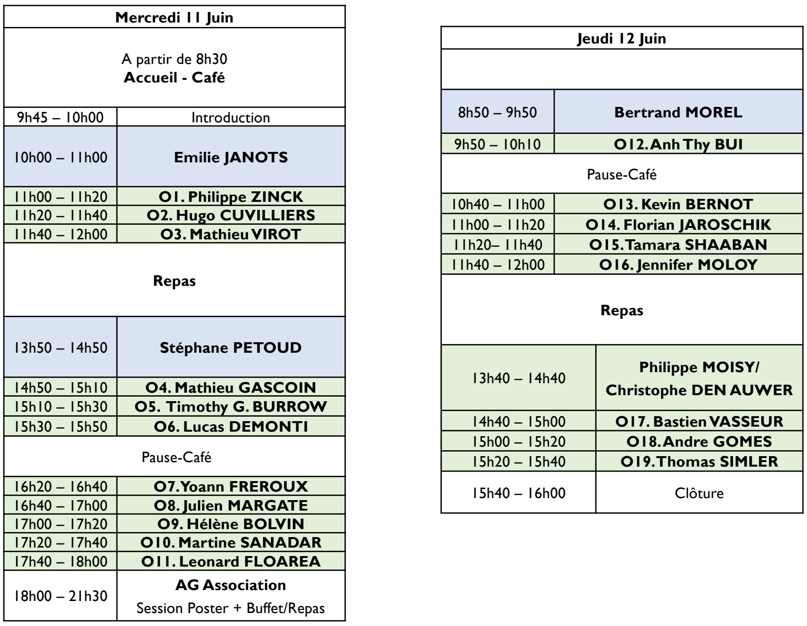
- Oral for Contributed Talk

- P for posters

- In the conference program, the **number** to the left is an hyperlink to abstract

Posters should be mounted upon arrival on Wedenesday and will remain on display until Thursday afternoon.

## PROGRAMME



| **Mercredi 11 Juin** | |
|---|---|
| A partir de 8h30<br>**Accueil - Café** | |
| 9h45 – 10h00 | Introduction |
| 10h00 – 11h00 | **Emilie JANOTS** |
| 11h00 – 11h20 | **O1. Philippe ZINCK** |
| 11h20 – 11h40 | **O2. Hugo CUVILLIERS** |
| 11h40 – 12h00 | **O3. Mathieu VIROT** |
| **Repas** | |
| 13h50 – 14h50 | **Stéphane PETOUD** |
| 14h50 – 15h10 | **O4. Mathieu GASCOIN** |
| 15h10 – 15h30 | **O5. Timothy G. BURROW** |
| 15h30 – 15h50 | **O6. Lucas DEMONTI** |
| Pause-Café | |
| 16h20 – 16h40 | **O7. Yoann FREROUX** |
| 16h40 – 17h00 | **O8. Julien MARGATE** |
| 17h00 – 17h20 | **O9. Hélène BOLVIN** |
| 17h20 – 17h40 | **O10. Martine SANADAR** |
| 17h40 – 18h00 | **O11. Leonard FLOREA** |
| 18h00 – 21h30 | **AG Association**<br>Session Poster + Buffet/Repas |

| **Jeudi 12 Juin** | |
|---|---|
| | |
| 8h50 – 9h50 | **Bertrand MOREL** |
| 9h50 – 10h10 | **O12. Anh Thy BUI** |
| Pause-Café | |
| 10h40 – 11h00 | **O13. Kevin BERNOT** |
| 11h00 – 11h20 | **O14. Florian JAROSCHIK** |
| 11h20– 11h40 | **O15. Tamara SHAABAN** |
| 11h40 – 12h00 | **O16. Jennifer MOLOY** |
| **Repas** | |
| 13h40 – 14h40 | **Philippe MOISY/ Christophe DEN AUWER** |
| 14h40 – 15h00 | **O17. Bastien VASSEUR** |
| 15h00 – 15h20 | **O18. Andre GOMES** |
| 15h20 – 15h40 | **O19. Thomas SIMLER** |
| 15h40 – 16h00 | Clôture |

| | **Intervenant** | **Title** | **Institution** |
|---|---|---|---|
| O1 | Philippe ZINCK | Yttrium Initiator For Chain Shuttling Polymerizations | UCCS Lille |
| O2 | Hugo CUVILLIERS | Influence De L'atmosphère Sur La Décomposition Thermique De L'oxalate De Cérium | UCCS Lille |
| O3 | Mathieu VIROT | Capturing A Hexanuclear Cluster Intermediate In The Formation Of $PuO_2$ Colloidal Nanoparticles | CEA Marcoules |
| O4 | Mathieu GASCOIN | Towards Describing f-element Complexes CPL Spectra Using Wavefunction Methods | ISCR Rennes |
| O5 | Timothy G. BURROW | Sensitivity To Cis- Versus Trans- Actinide-ligand Covalency In M4-edge Resonant Inelastic X-ray Scattering | Univ. Manchester, SOLEIL Gif-sur-Yvette |
| O6 | Lucas DEMONTI | Rare-earth Complexes With Hydrocarbon Ligands | LCM Palaiseau |
| O7 | Yoann FREROUX | New Antennae For Photoswitchable Luminescent Lanthanide(iii) Complexes | ISCR Rennes |
| O8 | Julien MARGATE | Reactivity Of $PuO_2$ Nanoparticles In The Presence Of $H_2O_2$: Sonochemical Insights And Peroxide Pathways | CEA Marcoules |
| O9 | Hélène BOLVIN | Hypersensitive Transitions In The Lnx3 Series | LCPQ Toulouse |
| O10 | Martine SANADAR | Can A Bioinspired Approach Enhance The Design Of A $Cu^{2+}$-responsive MRI Contrast Agent? | CBM Orléans |
| O11 | Leonard FLOAREA | Behaviour Of Uranyl Peroxocarbonate Complex After Oxidative Dissolution Of Potassium Uranates In Carbonate Media | UCCS Lille |
| O12 | Anh Thy BUI | TADF In Lanthanide Complexes: Leveraging Both Organic And f-element Photophysics | ISM Bordeaux |
| O13 | Kevin BERNOT | Lanthanide-based Supramolecular Nanotubes As New Platforms For Optical And Magnetic Nanodevices | INSA Rennes |
| O14 | Florian JAROSCHIK | Synthesis Of Linear Divalent Samarocenes Involving Spontaneous Sm(III)/Sm(II) Reduction Processes | ENSCM Montpellier |
| O15 | Tamara SHAABAN | Experimental Characterization And Theoretical Modelling Of X-ray Absorption Spectra Of Protactinium(V) Complexes | PhLAM Lille |
| O16 | Jennifer MOLLOY | Pro-radical Ligand-based Lanthanide Complexes As Molecular Redox Switches | Dpt Chimie Moléculaire Grenoble |
| O17 | Bastien VASSEUR | Towards Innovative Nuclear Reactors: Experimental Developments For The Characterization Of Chloride Actinides Salts | UCCS Lille |
| O18 | Andre GOMES | Core Excitations In Linear And Bent Uranyl Complexes | PhLAM Lille |
| O19 | Thomas SIMLER | H2 Splitting And N2 Hydrogenation Induced By A Divalent Lutetium Complex | LCM Palaiseau |

# CONFERENCE PROGRAM

## Wednesday, June 11th

### *9:45–10:00: Opening words*

### *10:00–12:00: Session 1*

7 **10:00** PL-1
*Emilie Janots (Institut des Sciences de la Terre – Grenoble)*
Les terres rares: ressource stratégique!

9 **11:00** Oral-1
*F. Bonnet, P. Zinck, X. Mosca, T. Bousquet, L. Pelinski, M. Bria (UMET, UCCS, Centre Commun de RMN, Université de Lille)*
Yttrium initiator for chain shuttling polymerizations

10 **11:20** Oral-2
*H. Cuvilliers, E. Capelli, B. Morel, M. Colmont, M. Rivenet (UCCS, UMR CNRS 8181, Cité Scientifique, Bât C7, 59652, Villeneuve d'Ascq Cedex, France)*
Influence de l'atmosphère sur la décomposition thermique de l'oxalate de cérium

11 **11:40** Oral-3
*M. Virot, M. Cot-Auriol, S. Dourdain, T. Dumas, C. Tamain, D. Menut, M.O.J.Y. Hunault, P. L. Solari, P. Moisy, S. I. Nikitenko (ICSM, Univ Montpellier, CEA, CNRS, ENSCM, Marcoule, France)*
Capturing a hexanuclear cluster intermediate in the formation of $PuO_2$ colloidal nanoparticles

### *Lunch*

### *13:50–15:50: Session 2*

12 **13:50** PL-2
*Stéphane Petoud (CBM – Orléans)*
Luminescent lanthanide compounds, optical spectroscopy and bioimaging

13 **14:30** Oral-4
*T. Burrows, Nathan M. Alcock, Myron S. Huzan, Myrtille O.J.Y. Hunault, Michael L. Baker (Department of Chemistry, The University of Manchester, Manchester, M13 9PL, UK; The University of Manchester at Harwell, Diamond Light Source, Harwell Campus, OX11 0DE, UK; Synchrotron SOLEIL, L'Orme des Merisiers, Saint-Aubin, BP48, 91190 Gif-sur-Yvette, France)*
Sensitivity to cis- versus trans- actinide-ligand Covalency in $M_4$-edge Resonant Inelastic X-ray Scattering

14 **14:50** Oral-5
*M. Gascoin, M. Grasser, G. David, B. Le Guennic (Univ Rennes, CNRS, ISCR (Institut des Sciences chimiques de Rennes) - UMR 6226, Rennes, France)*
Towards describing f-element complexes CPL spectra using wavefunction methods

15 **15:30** Oral-6
*L. Demonti, L. Pedaussaut, N. Mahieu, M. Mounir, N. Casaretto, G. Danoun, L. Maron, T. Simler, G. Nocton (LCM, CNRS, École Polytechnique, Institut Polytechnique de Paris, Palaiseau, France)*
Rare-earth complexes with hydrocarbon ligands

### *15:50–16:20: Pause Café*

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## *16:20–18:00: Session 3*

16 **16:20** Oral-7
*Yoann Fréroux, Salauat Kiraev, Akos Banyasz, Olivier Galangau, Olivier Maury, Stéphane Rigaut, Lucie Norel (Univ Rennes, CNRS, Institut des Sciences Chimiques de Rennes - UMR 6226, F-35000 Rennes, France)*
New antennae for photoswitchable luminescent lanthanide(III) complexes

17 **16:40** Oral-8
*J. Margate, S. I. Nikitenko, T. Dumas, S. Bayle, D. Menut, L. Bonato, E. Broussard, F. Moliere, L. Venault, M. Virot (ICSM, Univ Montpellier, CEA, CNRS, ENSCM, Marcoule, France)*
Reactivity of $PuO_2$ Nanoparticles in the Presence of $H_2O_2$: Sonochemical Insights and Peroxide Pathways

18 **17:00** Oral-9
*Hélène Bolvin (LCPQ, CNRS, Université de Toulouse, France)*
Hypersensitive transitions in the LnX3 series

19 **17:20** Oral-10
*M. Sanadar, K. Zimmeter, H. Martin, A. Pallier, F. Szeremeta, B. Vileno, P. Faller, A. Sour, C. Bonnet (Centre de Biophysique Moléculaire, CNRS UPR 4301, Université d'Orléans, Orléans, France)*
Can a bioinspired approach enhance the design of a $Cu^{2+}$-responsive MRI contrast agent?

20 **17:40** Oral-11
*L. Floarea, C. Coubronne, J. Margate, G. Milanole, M. Arab, V. Vallet, E. Berrier, M. Rivenet (Univ. Lille, CNRS, Centrale Lille, Univ. Artois, UMR 8181, UCCS - Unité de Catalyse et Chimie du Solide, Villeneuve d'Ascq, France)*
Behaviour of uranyl peroxocarbonate complex after oxidative dissolution of potassium uranates in carbonate media

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## *18:00–21:00: Session Poster*

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## *Poster contributions*

21 P-1
*Asma Allagui, A. Bouammali, Soufiane Tioul, Angus Shephard, Peter Junk, F. Jaroschik (Institut Charles Gerhardt Montpellier, Univ Montpellier, CNRS, ENSCM, Montpellier, France)*
Insights into the synthesis of divalent lanthanide complexes via selective C-P bond activation

22 P-2
*M. Berro, G. Danoun, G. Nocton (Laboratoire de Chimie Moléculaire, Ecole Polytechnique, Palaiseau, France)*
Photocatalytic drop-in biofuels production from fatty acids decarboxylation using uranyl nitrate

23 P-3
*Léo Chalaye, Salauat Kiraev, Amina Bensalah Ledoux, Stéphan Guy, Bruno Baguenard, Laure Guy, Olivier Maury (Laboratoire de Chimie CNRS UMR 5182, Ecole Normale Supérieure de Lyon, Lyon, France)*
Synthesis of lanthanide complexes for CPL applications

24 P-4
*Linda De Marchi, Angus Shephard, Lucie Pedussaut, Luca Demonti, Thayalan Rajeshkumar, Nicolas Casaretto, Laurent Maron, Grégory Danoun, Thomas Simler, Grégory Nocton (LCM, CNRS, Ecole Polytechnique, Institut Polytechnique de Paris, Palaiseau, France)*
Small molecule activation by low-valent uranium complexes

25 P-5
*D. Bhattacharjee, H.P. Singh, T. Simler, G. Nocton (LCM, CNRS, Ecole Polytechnique, Institut Polytechnique de Paris, Palaiseau, France)*
$CO_2$ fixation via low-coordinate $Ln(Cpttt)_2(BH_4)$ systems

26 P-6
*Yohan Champouret, Frederic Capet, Maxime Beauvois, Marc Visseaux (Univ. Lille, CNRS, Centrale Lille, Univ. Artois, UMR 8181 - UCCS, Lille, France)*
Versatile coordination chemistry of borohydride and allyl rare-earth complexes with amidopyridine ligands

27 P-7
*S. Duval, A. Flamant, C. Tamain, T. Loiseau (Univ. Lille, CNRS, Centrale Lille, Univ. Artois, UMR 8181 - UCCS, Lille, France)*
Hydrated lanthanide (La, Ce, Pr, Dy, Yb) pyromellitates 3D coordination polymer with tunnels encapsulating dimethylammonium species and its crystal-to-crystal transformation upon dehydration

28 P-8
*M. Maloubier, T. Shaaban, C. Le Naour, B. Siberchicot, F. Réal, V. Vallet (Université Paris-Saclay, CNRS/IN2P3, IJCLab, Orsay, France)*
Unraveling the unique chemistry of pentavalent protactinium: a singular actinide without the dioxo moiety

29 P-9
*O. Maury (CNRS, ENS de Lyon, Laboratoire de Chimie UMR 5182, Lyon, France)*
Unusual circularly polarized luminescence applications of f-elements

30 P-10
*M. Mounir, L. Demonti, N. Mahieu, G. Nocton (Laboratoire de Chimie Moléculaire (LCM), CNRS, Ecole Polytechnique, Institut polytechnique de Paris, Palaiseau, France)*
Design lanthanide dimeric complexes bridged by a nonaromatic $C_9H_{93}^{-}$ ligand

31 P-11
*L. De Marchi, L. Demonti, A. Combourieu, L. Pedussaut, E. Assendjee, M. Mounir, N. Mahieu, T. Simler, G. Danoun, G. Nocton (LCM, CNRS, Ecole Polytechnique, Institut Polytechnique de Paris, Palaiseau, France)*
Organometallic f-elements complexes for $N_2$ cleavage and photochemical reactivity

32 P-12
*Yoann Fréroux, Salauat Kiraev, Olivier Galangau, Tuan-Anh Phan, Olivier Maury, Stéphane Rigaut, Lucie Norel (Univ Rennes, CNRS, Institut des Sciences Chimiques de Rennes - UMR 6226, Rennes, France)*
Control of 4f complexes luminescence with organic photochromic units

33 P-13
*Sébastien Paloc (LCM, CNRS, Ecole Polytechnique, Institut Polytechnique de Paris, Palaiseau, France)*
Multimetallic organometallic complexes of uranium for ammonia synthesis

34 P-14
*Leonardo Papa, Olivier Maury, Amandine Roux, Sigolène Lecuyer (Univ. Lyon, École Normale Supérieure de Lyon, CNRS UMR 5182, Lyon, France)*
The imaging crystallophore, from protein crystals imaging to in vivo crystallization

35 P-15
*H. J. Sanderson, L. Pedaussaut, A. Shephard, T. Simler, G. Danoun, G. Nocton (LCM, CNRS, Ecole Polytechnique, Institut Polytechnique de Paris, Palaiseau, France)*
Large $\pi$-ligands for the synthesis of bimetallic lanthanide complexes

36 P-16
*H. P. Singh, N. Mahieu, L. Maron, G. Nocton, T. Simler (LCM, CNRS, Ecole Polytechnique, Institut Polytechnique de Paris, Palaiseau, France)*
CO-derived ethynediolato as a platform for small molecule functionalization

# Wednesday, June 12th

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## *8:50–10:10: Session 4*

37 **08:50** PL-3
*Bertrand Morel (Directeur R&D Orano)*
Chimie des éléments f dans le cycle du combustible

38 **09:50** Oral-12
*A.T. Bui, C. Ciambrone (Univ. Bordeaux, CNRS, Bordeaux INP, ISM, UMR 5255, F-33400 Talence, France)*
TADF in lanthanide complexes: leveraging both organic and f-element photophysics

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## *10:10–10:40: Pause Café*

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## *10:40–12:00: Session 5*

39 **10:40** Oral-13
*Bernot Kevin, F. Houard, E. Baranger, A. Gabbani, M. Albanesi, T. Guizouarn, Y. Suffren, G. Calvez, C. Daiguebonne, O. Guillou, F. Artzner, M. Mannini (Univ Rennes, INSA Rennes, CNRS, UMR 6226 ISCR, Université de Rennes, France)*
Lanthanide-based supramolecular nanotubes as new platforms for optical and magnetic nanodevices

40 **11:00** Oral-14
*R. P. Kelly, A. Bouammali, Z. Guo, T. Simler, L. Maron, G. B. Deacon, P. C. Junk, E. Jaroschik (School of Chemistry, Monash University, Clayton, Australia)*
Synthesis of linear divalent samarocenes involving spontaneous Sm(III)/Sm(II) reduction processes

41 **11:20** Oral-15
*T. Shaaban, C. Le Naour, H. Oher, T. Aubert, P. L. Solari, T. Burrow, M. Hunault, A.S.P. Gomes, F. Réal, V. Vallet, M. Maloubier (Université de Lille, CNRS, UMR 8523 - PhLAM, Lille, France)*
Experimental characterization and theoretical modelling of X-ray absorption spectra of protactinium(V) complexes

42 **11:40** Oral-16
*J. K. Molloy, A. Nhari, P. Beria, Florian Molton, O. Sénèque (Département de Chimie Moléculaire, Université Grenoble Alpes, CNRS, UGA, Grenoble, France)*
Pro-radical ligand-based lanthanide complexes as molecular redox switches

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## *12:00–13:40: Lunch*

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## *13:40–15:40: Session 6*

43 **13:40** PL-4
*Philippe Moisy / Christophe Den Auwer (CEA / Université Côte d'Azur*
Analogues chimiques aux éléments 5f

44 **14:40** Oral-17
*B. Vasseur, L. Hilaire, K. Perrin, J. Ocadiz, M. Rivenet (Univ. Lille, CNRS, Centrale Lille, Univ. Artois, UMR 8181 - UCCS, Lille, France)*
Towards innovative nuclear reactors: experimental developments for the characterization of chloride actinides salts

45 **15:00** Oral-18
*Andre Severo Pereira Gomes, Wilken Aldair Misael, Valerie Vallet (Univ. Lille, CNRS, UMR 8523 - PhLAM, Lille, France)*
Core excitations in linear and bent uranyl complexes

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**Journées Scientifiques 2025**

# YTTRIUM INITIATOR FOR CHAIN SHUTTLING POLYMERIZATIONS

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[2] *Unité de Catalyse et Chimie du Solide, UCCS, UMR8181, Université de Lille*

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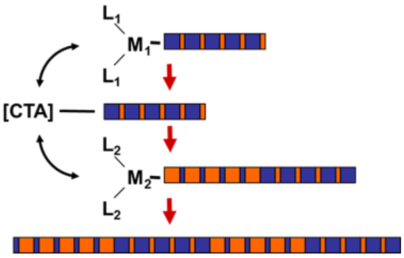

Chain shuttling copolymerization (CSP) is a powerful tool allowing the access to original multiblock copolymers in a one-pot one-step route.[1] The growing macromolecular chain is allowed to "shuttle" via a chain transfer agent (CTA) between two catalysts presenting a difference in comonomers reactivity ratios, and thus leading to statistical copolymeric blocks of different composition. We have extended this process initially developed for polyolefins [1] to the ring opening copolymerization of cyclic esters, namely L-lactide and ε-caprolactone, affording the access to new biobased multiblock copolymers.[2] This was initially done using aluminium based initiators that are particularly well suited for ring-opening polymerization. The control of the selectivity is a key point in this chemistry when it comes to materials properties. The yttrium oxide alkoxide $Y_5(\mu\text{-}O)(OiPr)_{13}$ is known for its extremely high selectivity for lactide in lactide / ε-caprolactone statistical copolymerizations. [3] The replacement of one of the aluminum complexes by the $Y_5(\mu\text{-}O)(OiPr)_{13}$ initiator in the chain shuttling copolymerization has enabled to form hard blocks highly enriched in L-lactide and soft blocks enriched in ε-caprolactone, respectively, thereby improving significantly the thermal and mechanical properties of the resulting materials.[4]

**Acknowledgments** : The ANR is gratefully acknowledged for funding this projet (PLANAVETTE - ANR-21-CE06-0024)

References

[1] D. J. Arriola, E. Carnahan, P. D. Hustad, R. L. Kuhlman and T. T. Wenzel, *Science*, **2006**, *312*, 714
[2] J. Meimoun, C. Sutapin, G. Stoclet, A. Huret, P. Roussel, M. Bria, S. Chirachanchai, F. Bonnet, P. Zinck, *J. Am. Chem. Soc.* **2021**, *143*, 21206
[3] W. M. Stevels, M. J. K. Ankoné, P. J. Dijkstra and J. Feijen, *Macromolecules*, **1996**, *29*, 6132
[4] X. Mosca, L. Perchery, M. Bria, J. D. Winter, G. Stoclet, T. Bousquet, L. Pelinski, F. Bonnet, P. Zinck, *Polym. Chem.*, **2024**, *15*, 4020

CenTRA **Journées Scientifiques 2025**

# INFLUENCE DE L'ATMOSPHÈRE SUR LA DÉCOMPOSITION THERMIQUE DE L'OXALATE DE CÉRIUM

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Ce travail se concentre sur la décomposition thermique de l'oxalate de cérium, utilisé comme analogue dans le but d'éclairer les mécanismes réactionnels à l'origine de la synthèse du $PuCl_3$ à partir de l'oxalate de plutonium trivalent [1]. Si la décomposition de l'oxalate de cérium sous argon est bien connue, se décomposant d'abord en oxocarbonate puis en oxyde [2], elle est beaucoup moins bien comprise sous HCl. Afin de faire la lumière sur les mécanismes de chloration, un montage expérimental a été développé, la décomposition thermique de l'oxalate de cérium a été étudiée sous différentes atmosphères : Ar, Ar + $H_2$ et HCl en mélange avec Ar ou Ar + $H_2$ et les intermédiaires de décomposition ont été analysés par diffraction X, spectroscopie (Infra-Rouge, Raman), fluorescence X et analyse thermique. D'après les résultats obtenus, l'ajout de dihydrogène (2,9 %) n'affecte pas le schéma de décomposition et conduit aux mêmes intermédiaires et au même composé final que sous argon. La décomposition sous HCl diffère de manière significative. Pour certaines conditions particulières, le produit obtenu correspond à une phase originale qui consiste en des cristaux gris insolubles dans l'eau. Les données de spectroscopie Infra-Rouge recueillies sur la poudre indiquent que la phase est anhydre et conserve globalement la signature de l'oxalate de cérium initial assortie de deux signaux supplémentaires situés à 1730 $cm^{-1}$ et 1355 $cm^{-1}$, ainsi que des pics beaucoup plus fins. Par analyse ATG-MS sous argon, la décomposition de cette nouvelle phase montre un profil de perte de masse proche de celui de l'oxalate de cérium anhydre, accompagné d'un dégagement de $CO_2$ et de CO. En fin de décomposition, un mélange de $CeO_2$ et d'amorphe est obtenu et la perte de masse enregistrée est de -27 %, une valeur éloignée de la perte de masse théorique de l'oxalate de cérium anhydre (-37 %) décomposé en oxyde. L'étude de cette phase inconnue a donc été approfondie et la présentation se concentrera plus spécifiquement sur son identification.

## References

[1] K. Harmon, E. Wichers. *United States Patent Office* **1961**.
[2] L. De Almeida, *et al. Eur. J. Inorg. Chem.* **2012**, *31*, 4986-4999.

CenTRA **Journées Scientifiques 2025**

# CAPTURING A HEXANUCLEAR CLUSTER INTERMEDIATE IN THE FORMATION OF $PuO_2$ COLLOIDAL NANOPARTICLES

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M.O.J.Y. Hunault,[3] P. L. Solari,[3] P. Moisy,[2] S. I. Nikitenko,[1]

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Characterizing the structure and formation pathway of plutonium oxide ($PuO_2$) nanoparticles in aqueous solution is essential for addressing challenges in nuclear waste management, environmental safety, and the development of advanced actinide-based materials.[1-3] Despite extensive structural characterization of oxide nanoparticles derived from Pu(IV) hydrolysis, insights into the underlying formation mechanisms remain limited.[2] Recent research has highlighted the potential role of transient Pu(IV) polynuclear clusters as key intermediates in the formation of colloidal $PuO_2$ nanoparticles.[4] These species, stabilized under specific conditions, offer a unique opportunity to investigate the physicochemical pathways governing nanoparticle nucleation and growth.

This work focuses on elucidating the formation mechanisms of $PuO_2$ nanoparticles in aqueous solution through a combination of laboratory and synchrotron-based techniques. Vis-NIR absorption spectroscopy conducted during plutonium hydrolysis in various aqueous media ($H_2O$, $D_2O$, DOTA, glycine, acetate) has revealed spectral features corresponding to stabilized intermediate species. Small-angle X-ray scattering (SAXS) and X-ray absorption spectroscopy (XAS) were employed to probe their nanoscale structure and electronic environment, providing clear evidence for the involvement of hexameric Pu(IV) oxo-hydroxo clusters. These findings offer direct experimental insight into the early stages of $PuO_2$ nanoparticle formation and support the hypothesis that discrete polynuclear species serve as precursors to crystalline, nanoscale $PuO_2$ colloids.

Beyond its significant contribution to the fundamental understanding of plutonium chemistry in aqueous media, this work also demonstrates the added value of synchrotron radiation for characterizing highly dilute and strongly radioactive actinide nanostructures, paving the way for further research in this field.

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# Sensitivity to cis- versus trans- actinide-ligand Covalency in $M_4$-edge Resonant Inelastic X-ray Scattering

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The determination of actinide electronic structure is becoming increasingly more synonymous with high energy resolution fluorescence detected (HERFD) x-ray spectroscopy, with spectra composed of fine structure advantageously obtained from the increased resolution corresponding to final state core-holes with larger lifetimes [1-4]. The fine structure acquired allows for the evaluation of oxidation states and the respective local coordination. HERFD measurements, alone though, provide partial insights, with respect to all phenomena present.

To build upon the foundational information of HERFD spectra, new analysis protocols concerning actinide 3d4f resonant inelastic x-ray scattering (RIXS) measurements, probing the unoccupied 5f orbitals, will be discussed. The proposed protocol accounts for all intensity as a function of the photon-in photon-out inelastic scattering transitions. Interpretation of RIXS spectra measured on model air-sensitive uranium complexes at the MARS beamline of Synchrotron SOLEIL will be presented, along with complementary multiplet theory and density functional theory calculations. This analysis provides comprehensive insights into what can be extracted from actinide 3d4f RIXS data. It will be discussed how RIXS can be used to determine electronic structure, while emphasising how the technique is sensitive to cis- versus trans- covalency, occurring between the actinide 5f orbitals and ligand valence orbitals [1].

Interpretation of the presented RIXS spectra will be discussed considering insights from ligand K-edge x-ray absorption spectroscopy amongst others [5,6].

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**Journées Scientifiques 2025**

# TOWARDS DESCRIBING F-ELEMENT COMPLEXES CPL SPECTRA USING WAVEFUNCTION METHODS

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Lanthanides complexes exhibit remarkable optical properties, with large applications in luminescent devices. Their intra-4f transitions produce sharp and well-defined emission lines, spanning from the ultraviolet to the near-infrared, depending on the specific $Ln^{3+}$ ion involved.

When chirality is introduced—typically through the coordination environment—the polarization of the light emitted by the lanthnide ion can be significantly affected. Electric dipole-forbidden but magnetic dipole-allowed 4f–4f transitions give rise to Circularly Polarized Luminescence (CPL), corresponding to the differential emission of left- and right-circularly polarized light.

A thorough understanding of CPL spectra requires the support of theoretical chemistry tools. However, accurately modeling the luminescent properties of lanthanide ions remains a methodological challenge in quantum chemistry due to their open-shell electronic structure and strong spin–orbit coupling.

In this work, we employ wavefunction-based quantum chemistry methods (CASSCF, CASPT2, SI-SO) to simulate the CPL spectra of various lanthanide complexes, and compare the computed results with experimental data. We discuss the remaining methodological challenges and present the development of a computational protocol designed to extend CPL simulation capabilities to actinide complexes.

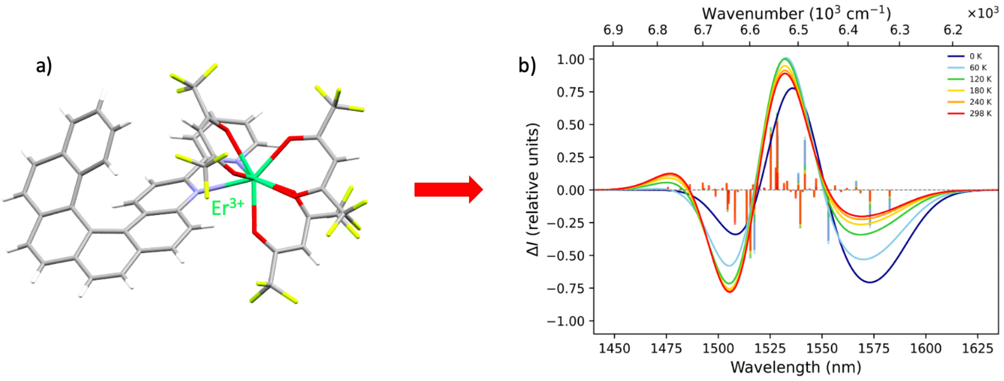

*Figure 1. a) Structure of a chiral molecular complex of trivalent erbium. b) Associated calculated CPL spectrum as a function of the temperature.*

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# RARE-EARTH COMPLEXES WITH HYDROCARBON LIGANDS

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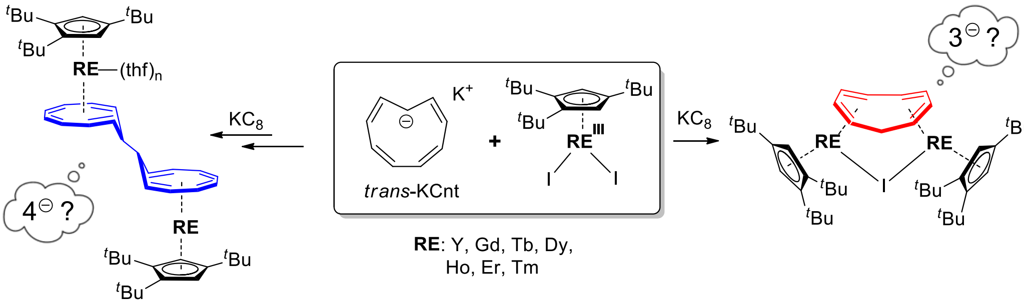
The chemistry of f-elements with aromatic ligands has been extensively studied over the past decades,[1] yet it continues to yield novel and intriguing compounds.[2] The most widely used scaffolds for such chemistry are the relatively small monoanionic cyclopentadienyl ring ($Cp^-$)[3a] and the considerably larger dianionic cyclooctatetraenyl ligand ($COT^{2-}$),[3b] which provided access to a vast array of compounds with unique physical and chemical properties.

A relatively new addition to this family of ligands is the larger monoanionic cyclononatetraenyl ring ($Cnt^-$). Although known since the 1960s, this nine-membered 10π-electron carbocycle has been introduced in lanthanide chemistry only relatively recently in 2017.[4] In the short span of eight years, a family of lanthanide complexes bearing the Cnt ligand has been reported, highlighting different possible coordination modes to the metal centre[5] and peculiar light-induced reactivity.[6]



**RE**: Y, Gd, Tb, Dy, Ho, Er, Tm

**Figure: Cnt reactivity for the coordination to RE complexes in reducing conditions**

However, the distinctive properties and reactivity of such ligand remain largely unexplored. Under reducing conditions, the Cnt ligand seems to be able to accommodate more electrons on the π-system, leading to the formation of dimeric bridging species or to homocoupling reactions. Such reactivity allows the synthesis and isolation of unique lanthanide species.

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**Journées Scientifiques 2025**

# NEW ANTENNAE FOR PHOTOSWITCHABLE LUMINESCENT LANTHANIDE(III) COMPLEXES

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Lanthanide(III)-based complexes are widely used due to their original emission features such as long-lived and narrow bandwidth luminescence from the visible up to the near infrared spectral range.[1] Photomodulation of this emission is a fundamental challenge, which has been mostly achieved with visible light emitting Eu(III) complexes, whereas our research group more recently achieved photoswitchable NIR luminescent lanthanide(III) complexes.[2]

To this end, we have previously designed a new ligand bearing a dithienylethene (DTE) moiety, efficient for quenching the luminescence of lanthanide(III) complexes by energy transfer in only one of its two states, even in the NIR region, paving the way for applications ranging from anti-counterfeiting systems to super-resolution microscopy. However, at this stage, these systems suffer from low brightness and present only destructive readout.[3]

Here, we present a new strategy based on new boranil-based lanthanide(III) complexes displaying (i) an improved brightness with a high on/off intensity quenching ratio, (ii) an antenna effect leading to lanthanide ion NIR emission (Ln = Yb, Er) with a non-destructive readout through selective visible light excitation in the boranil centered absorption band.

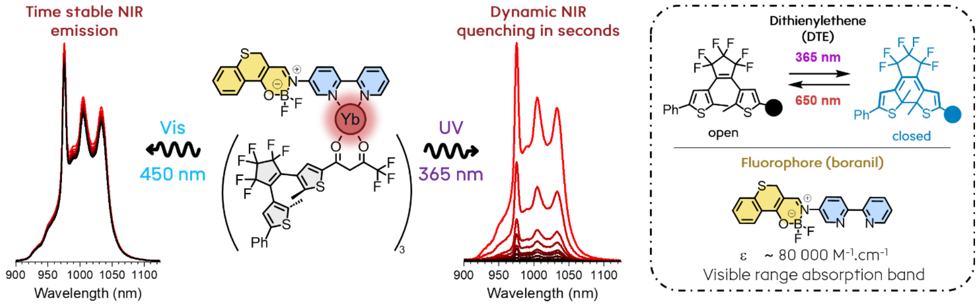

**Figure 1.** An Ytterbium(III) complex combining photochromic DTE ligands and a fluorophore as an antenna provides efficient luminescence switching with non-destructive readout behaviour.

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Journées Scientifiques 2025

# Reactivity of $PuO_2$ Nanoparticles in the Presence of $H_2O_2$: Sonochemical Insights and Peroxide Pathways

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Plutonium dioxide ($PuO_2$) is known for its very low solubility in water, especially in its bulk form. However, when reduced to the nanoscale, its surface properties can change, making it more reactive under specific conditions **[1]**. In geological nuclear waste storage, the radiolysis of water produces reactive species such as $H_2O_2$, which can significantly impact the long-term stability of spent fuel materials **[2]**. Sonochemistry, through acoustic cavitation, enables the controlled generation of $H_2O_2$ in aqueous systems, offering a relevant method to probe actinide reactivity under conditions simulating radiolytic environments **[3]**.

Ultrasound has previously been shown to promote the formation of actinide peroxides, particularly with uranium and thorium, revealing unexpected redox pathways and demonstrating the potential of sonochemistry to explore actinide reactivity **[4-5]**. In this study, we apply sonochemistry to investigate the reactivity of $PuO_2$ nanoparticles in pure water under an Ar/(20%)$O_2$ atmosphere. Curiously, the $PuO_2$ colloids showed clear signs of reactivity under ultrasound with partial dissolution of $PuO_2$ nanoparticles, leading to the formation of stable and potentially mobile plutonium species, such as Pu(IV) peroxo complexes **[6]**. These findings offer new insights into the environmental behavior of $PuO_2$ NPs, particularly under radiolytic conditions where $H_2O_2$ may accumulate. This has significant implications for long-term nuclear waste stability and plutonium remediation strategies.

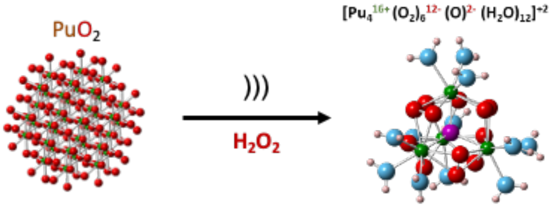

Figure 1 : Schematic Pathway for the Sonochemical and $H_2O_2$-Induced Conversion of $PuO_2$ Nanoparticles into a Pu(IV) Peroxide Species

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CenTRA **Journées Scientifiques 2025**

# Hypersensitive transitions in the $LnX_3$ series.

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While f-f transitions in lanthanide complexes are Laporte forbidden, some transitions in the non-centrosymmetric complexes, denoted *hypersensitive*, are strongly exalted and highly sensitive to changes in symmetry, polarizability, and coordination geometry of the ligands.

In this presentation, we will present a strategy to calculate from first-principles the absorption spectra in the lanthanide trihalide series based on the *dynamic coupling model* [1]. The calculated hypersensitive transitions are in excellent agreement with the available experimental data (Ln = Pr, Nd, Er, Tm) [2].

The Judd-Ofelt parameters are calculated for all complexes and we will discuss the trends in terms of the metal and the halide. We calculated from first principles the crystal-field parameters in the 4f subspace, as well for the 4f-5d spaces, in order to discuss the Judd-Ofelt theory [3] which is based on those crystal-field parameters of odd orders.

Finally, we will analyze the effect of temperature.

**Acknowledgements.**

This work was initiated by essential and stimulating discussions with Claude Piguet (Geneva) and Jean-Claude Bünzli (Lausanne).

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**Journées Scientifiques 2025**

# CAN A BIOINSPIRED APPROACH ENHANCE THE DESIGN OF A CU$^{2+}$-RESPONSIVE MRI CONTRAST AGENT?

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Imaging extracellular $Cu^{2+}$ *in vivo* is important due to its role in physiological and pathological processes.[1] Magnetic resonance imaging is a promising modality for this purpose but developing contrast agents selective for $Cu^{2+}$ over abundant $Zn^{2+}$ ions remains a challenge.[2] We synthesized and characterized three novel ligands,[3] DO3A-pyrGH/-picG/-picGH (Fig. 1), containing a macrocycle and a pendant arm for $Cu^{2+}$ complexation inspired from the ATCUN site of human serum albumin. The corresponding $Ln^{3+}$ complexes were studied in the presence and in the absence of $Cu^{2+}$ through UV-visible, fluorescence and EPR spectroscopies, as well as relaxivity measurements. These studies showed that Gd-DO3A-picG and Gd-DO3A-picGH are non-hydrated complexes, in which the pyridine-amide moiety remains coordinated to $Ln^{3+}$ even in the presence of $Cu^{2+}$. Although Gd-DO3A-picG does not respond to $Cu^{2+}$, a sizeable relaxivity increase is observed for Gd-DO3A-picGH. While Gd-DO3A-pyrGH showed a remarkable increase in relaxivity of nearly 400% in the presence of $Cu^{2+}$, which could be rationalized in terms of an increase in the hydration number of the $Ln^{3+}$ ion. Importantly, the system also displayed an unprecedented selectivity for $Cu^{2+}$ over $Zn^{2+}$ which lies directly in the bioinspired design.

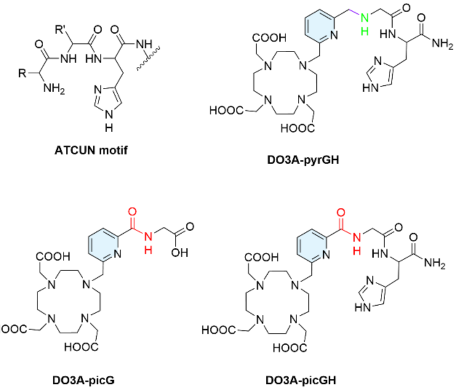

**Figure 1: Chemical structure of the discussed complexes.**

**We acknowledge the support from the Agence Nationale pour la recherche (grantANR-22-CE07-0030).**

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Journées Scientifiques 2025

# BEHAVIOUR OF URANYL PEROXOCARBONATE COMPLEX AFTER OXIDATIVE DISSOLUTION OF POTASSIUM URANATES IN CARBONATE MEDIA

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Different effluents and mine tailings are treated with potash, KOH, throughout the stages of the front end of the French nuclear fuel cycle, thus forming large quantities of valuable U-based materials, awaiting suitable reprocessing and further valorization. In these materials, the uranium is forming a mixed oxide together with the $K^+$ ions, more commonly known as potassium uranates group or KDU. The dissolution in an alkaline oxidizing solution, such as $CO_3^{2-}$ – $H_2O_2$ environment, already shown a powerful new way of recovering uranium from several materials [1, 2]. Thus, by means of a peroxocarbonate route, uranium from KDUs is supposed to preferentially dissolve and form the uranyl peroxocarbonate complex $[UO_2(O_2)(CO_3)_2]^{4-}$, together with other complexes, according to the following reaction :

$$U_2O_7^{2-} + 2yCO_3^{2-} + 2xO_2^{2-} + 6H_3O^+ \rightarrow 2[UO_2(O_2)_x(CO_3)_y]^{2-2x-2y} + 9H_2O$$

This study aims to identify the role of the carbonate source's counter-cation in the solubility of KDU and the stability of the $[UO_2(O_2)(CO_3)_2]^{4-}$ complex. The dissolution media are prepared by either using a mixture of $M_2CO_3$ and $H_2O_2$ (M=Na, K, $NH_4$), or the sodium carbonate perhydrate, $Na_2CO_3 \cdot 1{,}5H_2O_2$, and various molar ratio $[CO_3^{2-}]:[H_2O_2]:[U]$ are used. The working concentration of uranium is fixed to 50 g/L and measured experimentally by ICP-AES and X-ray fluorescence. The different solutions are analyzed by Raman spectroscopy in order to investigate the uranyl speciation and the measured vibrational bands are compared with those obtained by DFT calculations and those measured previously by Kim *et al.* [3]. Based on the first results, the counter-cation of the carbonate source has a drastic effect on the dissolution kinetics, the use of $(NH_4)_2CO_3$ conducting to the maximal solubility of KDU. However, by coupling chemical modelling calculations and Raman spectroscopy data, an improved stability of the target complex was identified in $Na_2CO_3$-based solutions.

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# INSIGHTS INTO THE SYNTHESIS OF DIVALENT LANTHANIDE COMPLEXES VIA SELECTIVE C-P BOND ACTIVATION

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In our on-going research on the synthesis of divalent organolanthanide complexes bearing bulky polyarylcyclopentadienyl ligands,[1-3] we have recently reported an efficient strategy involving selective carbon-phosphorous bond cleavage in cyclopentadiene-phosphine precursors using zero-valent lanthanide metals (Figure 1).[4] In order to get a better mechanistic understanding on the underlying reaction process and prepare the extension of this methodology to non-classical divalent lanthanides, several modifications of the Cp-phospine framework have been undertaken. We herein report our findings using new P(III) and P(V) derivatives, which helped to gain new insights in the scope and mechanism of this reaction.

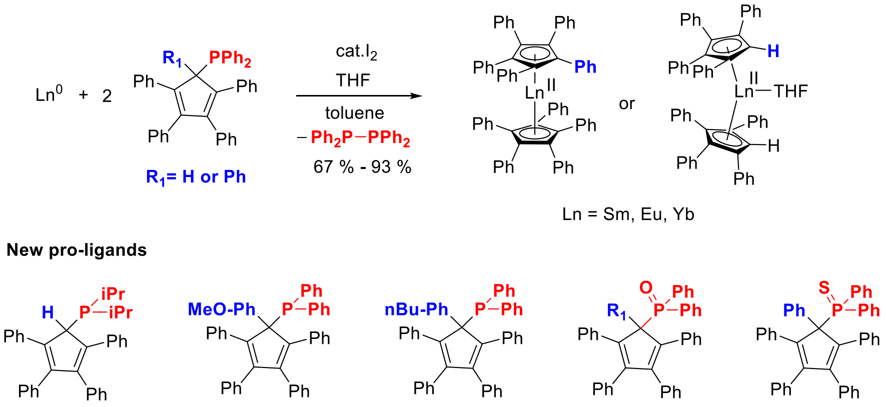

**Figure 1 :** New P(III) and P(V) derivatives applied for the synthesis of divalent lanthanide complexes involving selective C-P bond cleavage.

**Acknowledgements.**

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# PHOTOCATALYTIC DROP-IN BIOFUELS PRODUCTION FROM FATTY ACIDS DECARBOXYLATION USING URANYL NITRATE

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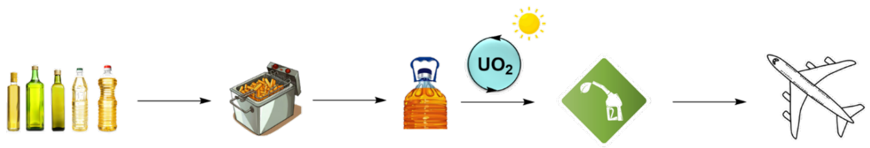
Fossil fuels energy production is a significant contributor to the global temperature increase, primarily due to the production of $CO_2$. Alternative sustainable energy sources have been developed in the last decades to replace fossil fuels consumption. Biodiesel is considered a conventional option. However, due to its cold flow properties and poor storage stability, biodiesel is regarded as a less-than-ideal transportation fuel. As a result, attention has shifted to green hydrocarbons. These biofuels have equivalent performance characteristics to fossil fuel making them compatible with modern motors. Additionally, they can be easily obtained from sustainable resources, such as vegetable oils and bio-derivatives [1].

Nevertheless, traditional thermal catalytic systems often require harsh conditions, reducing the overall sustainability of these processes. Alternative pathways have been proposed such as photocatalytic hydrodecarboxylation of bioderived fatty acids to obtain hydrocarbons. Despite the advancement in current photocatalytic systems, they still have their drawbacks including the use of expensive photocatalysts, the need for stoichiometric amounts of base, and the incorporation of various additives. Therefore, alternative photocatalysts are essential for a more sustainable approach. Depleted uranium, a mildly radioactive by-product of $^{235}U$ enrichment, can be considered an ideal photocatalyst for light-driven photo-redox reactions [2]. In this context, depleted uranium can serve as a replacement for rare and expensive catalysts.

Herein, we report the first investigation into the use of depleted uranium for the decarboxylation of long-chain fatty acids into $C_{n-1}$ alkanes. We are pleased to announce that this photocatalytic system operates at mild conditions, utilizing water as a sole additive, and using a minimal amount of photocatalyst.



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**Journées Scientifiques 2025**

# SYNTHESIS OF *LANTHANIDE* COMPLEXES FOR CPL APPLICATIONS

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Lanthanide complexes are well-known for their characteristic f–f forbidden transitions, leading to sharp emission bands and long luminescence lifetimes. Among these transitions, some are magnetic dipole-allowed, making the lanthanide complexes particularly attractive for applications involving Circularly Polarized Luminescence (CPL).[1]

CPL is the differential emission of left- and right-circularly polarized light by chiral emitters. Its intensity is quantified by the dissymmetry factor (glum), with values ranging between –2 and +2.[2]

In this context, Gunnlaugsson's pyridine-diamide ligands are interesting due to their ability to form stable, chiral helical complexes with lanthanide ions. These chiral complexes have shown good CPL properties with reported glum values up to 0.3.[3]

The goal of this project is to synthesize chiral lanthanide complexes, designed for incorporation into materials. Based on the Gunnlaugsson scaffold, the ligands are modified with light-harvesting antennae to improve excitation efficiency and to change the properties of the resulting materials.

Finally, the integration of these chiral complexes into materials such as PDMS aims to develop new standards for CPL microscopy and to create mechanically responsive systems.

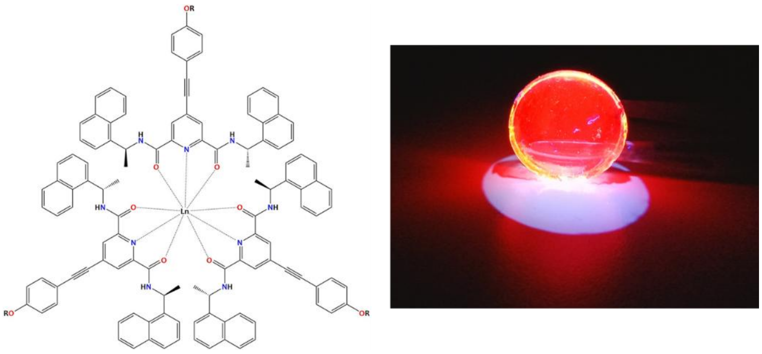

**Figure:** Structure of the synthesised chiral lanthanide complexes (left) and PDMS disk incorporating synthesised europium complex under UV light (right).

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**Journées Scientifiques 2025**

# SMALL MOLECULE ACTIVATION BY LOW-VALENT URANIUM COMPLEXES

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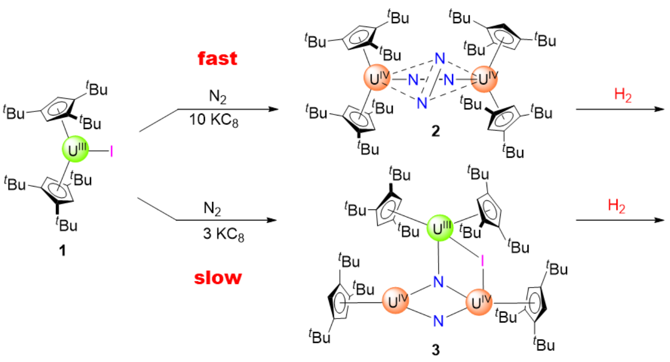
Ammonia ($NH_3$) represents a fundamental nitrogen source for nitrogen-based fertilizers in agriculture. It has recently been considered an alternative way to store hydrogen, particularly for marine fuels. Nevertheless, the Haber-Bosh process used to produce $NH_3$ from $N_2$ and $H_2$ requires harsh temperature and pressure conditions. Given the current energetic context, researchers are investigating novel strategies to convert these broadly available molecules under mild conditions.[1]
One of the challenges is represented by the high dissociation energy of $N_2$ (945.33 ± 0.59 kJ.mol$^{-1}$).[2] In this context, Uranium organometallic complexes have been extensively studied in light of the reduction potential of low-valent Uranium species and the rich redox chemistry of Uranium.[3]



Herein, we present how the known U(Cpttt)$_2$I[4] (Cp$^{ttt}$ = 1,2,4-tris(*tert*-butyl)cyclopentadienyl), in the presence of an external reductant, can activate $N_2$ with relatively fast kinetics at room temperature and atmospheric pressure, affording different structural motifs (**2** and **3**) depending on the amount of $KC_8$ present. We will also present the reaction with $H_2$ of both complexes and the following protonolysis reaction to afford $NH_4Cl$.

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CenTRA Journées Scientifiques 2025

# $CO_2$ FIXATION VIA LOW-COORDINATE LN($CP^{TTT}$)$_2$($BH_4$) SYSTEMS

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To trap and transform $CO_2$, complexes based on metal hydrides are promising candidates. For example, molecular assemblies based on zinc hydrides have been shown to react reversibly with $CO_2$ very recently, allowing for direct air capture at high temperatures.[1]

In this context, lanthanide organo-borohydride complexes featuring sterically demanding cyclopentadienyl ligands can exhibit similar reactivity towards small molecules. In this work, [La($Cp^{ttt}$)$_2$($BH_4$)] and [Ce($Cp^{ttt}$)$_2$($BH_4$)] were synthesized via salt metathesis from [Ln($BH_4$)$_3$($THF$)$_n$] and $KCp^{ttt}$, following established procedures.[2][3] Reactivity with $CO_2$ revealed insertion of $CO_2$ into the Ln–$BH_4$ bond, resulting in dimeric formate-bridged products of the type [($Cp^{ttt}$)$_2$Ln(m-$O_2CH$)$_2$Ln($Cp^{ttt}$)$_2$] (Ln = La, Ce). The de-coordination of the formate ligand was investigated with different boron-based reagents.

These results expand the scope of $CO_2$ functionalisation in f-block chemistry and open new avenues for $CO_2$ trapping and transformation.

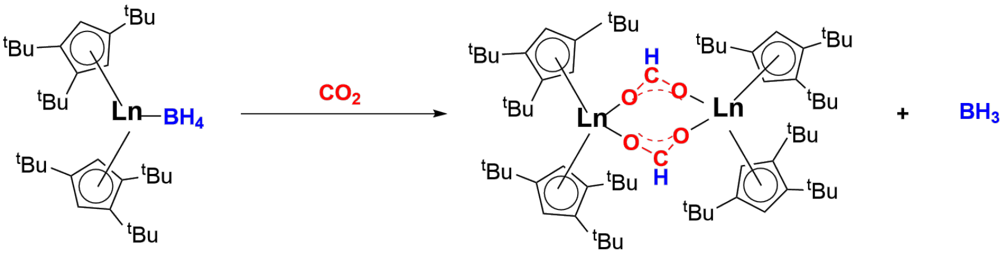

**Figure:** Trapping of $CO_2$ by a $Ln^{III}$ borohydride complex.

**Acknowledgements.**

The Fondation de l'X has funded part of this work.

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CenTRA Journées Scientifiques 2025

# VERSATILE COORDINATION CHEMISTRY OF BOROHYDRIDE AND ALLYL RARE-EARTH COMPLEXES WITH AMIDOPYRIDINE LIGANDS

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Amido-pyridine ligands are attractive due to the easy access to the protonated amino counterpart (pro-ligand: ZH) through a simple condensation reaction of a suitable amine on the pyridyl ketone, followed by a reduction reaction of the imine group.[1] These ligands offer the possibility to be modified at various sites, such as the substituent on the pyridine ring, the group on the carbon in the α-position of the amine, and the substituent carried by the amine nitrogen, allowing for a rich variation of coordination and electronic/steric properties of the resulting metal complex.

In recent years, the coordination chemistry of borohydride and allyl groups in rare-earth complexes of the type [RE]-($BH_4$)[2] or [RE]-($C_3H_5$)[3] has received significant interest and has been recognized as offering high potential for various catalytic transformations. In this study, a new family of rare-earth metal borohydride[4] and allyl complexes supported by amido-pyridine ligands was developed in our research group (Figure). These complexes were found to be very versatile in terms of coordination mode with neodymium (and also yttrium), producing complexes with good abilities for the ring-opening polymerization of cyclic esters.

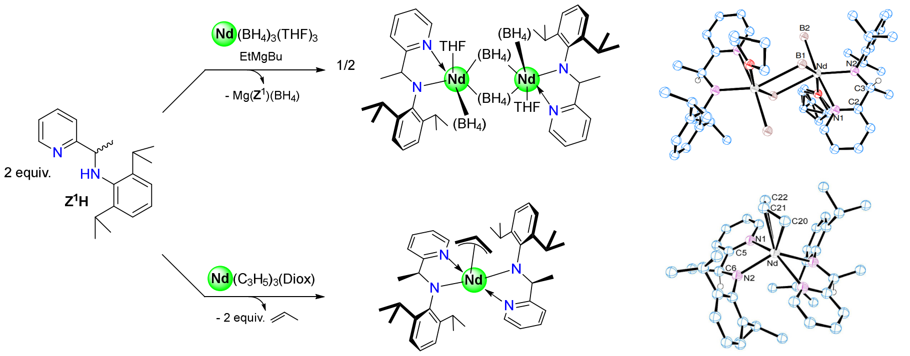

**Figure:** Examples of coordination chemistry of Nd borohydride and Nd allyl with amido-pyridine ligand $\mathbf{Z^1}$

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**Journées Scientifiques 2025**

# HYDRATED LANTHANIDE (LA, CE, PR, DY, YB) PYROMELLITATES 3D COORDINATION POLYMER WITH TUNNELS ENCAPSULATING DIMETHYLAMMONIUM SPECIES AND ITS CRYSTAL-TO-CRYSTAL TRANSFORMATION UPON DEHYDRATION

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The solvothermal synthesis and characterization of two distinct structural types of coordination polymers are reported with 1,2,4,5-benzenetetracarboxylate (pyromellitate, noted btec) ligands associated to light lanthanides (Ln) Ce(III), La(III) and Pr(III) for compounds **1**, **2** and **3**, and heavy lanthanides Dy(III) and Yb(III) for compounds **4** and **5**, respectively. The two structures are built up from the connection lanthanide centers with the btec linkers in order to construct 3D framework composed of 1D tunnels encapsulating dimethylammonium and water molecules in $[\mathrm{Ln(btec)}]\cdot\mathrm{HDMA}\cdot 2\mathrm{H_2O}$ (compounds **1**-**3**) or dimethylammonium only in $[\mathrm{Ln(btec)(H_2O)}]\cdot\mathrm{HDMA}$ (compound **4** & **5**). These two atomic arrangements differ by 1) the occurrence of infinite chains of edge-sharing $\{\mathrm{LnO_9}\}$ units in **1**-**3**, instead of dinuclear carboxylate bridged $\{2 \times \mathrm{LnO_8}\}$ units in **4**-**5**; and 2) the presence of trapped water species in **1**-**3**, instead of bonded aquo species to Ln centers in **4**-**5**. The dehydration process has been particularly investigated for the cerium-containing solid: the removal of the water molecule (up to 120°C) induces a crystalline phase transition related to the shrinkage of the 3D network, corresponding to the spatial matching of the channel with the remaining cationic dimethylammonium species in the form ($[\mathrm{Ln(btec)}]\cdot\mathrm{HDMA}$, noted **1'**). This single-crystal to single-crystal transformation thus shows a relative flexibility of the network as shown by the cell volume $\Delta V$ variation of -6%, and is reminiscent to the breathing effect reported in well-known MOF materials such the MIL-53 series.

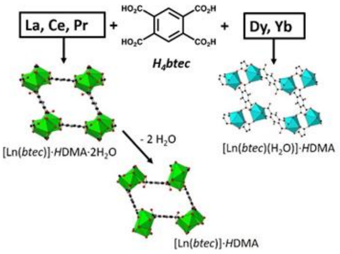

**Figure 1: SCXRD structure of {Ln(btec)} coordination polymers and the crystalline phase transition in {Ce(btec)}**

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**Journées Scientifiques 2025**

# UNRAVELING THE UNIQUE CHEMISTRY OF PENTAVALENT PROTACTINIUM: A SINGULAR ACTINIDE WITHOUT THE DIOXO MOIETY

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Protactinium(V) stands out among the actinides(V) due to its unique chemical behavior, characterized by the absence of the actinyl moiety in condensed phase compounds. Instead, Pa(V) features a short mono-oxo bond, experimentally observed in oxalic and sulfuric media. However, the stability of this bond is uncertain and can disappear upon complexation, as seen with fluoride ions [1]. Interestingly, the experimentally measured Pa-O bond length in oxalate complexes (1.75 Å) significantly differs from the theoretical prediction of ~ 1.85 Å [2], highlighting the challenges in accurately modelling Pa(V) behavior. The study of Pa(V) is further complicated by its remarkable propensity for hydrolysis and polymerization, even under acidic conditions, and the difficulty in isolating significant amounts of this actinide, making it challenging to handle and investigate.

In this study, we investigate the complexation of Pa(V) with chloride ions, using x-ray absorption spectroscopy (XAS) to probe its chemical environment in varying concentrations of hydrochloric acid. Chlorides, with their weak ligating properties, are expected to stabilize the mono-oxo bond in Pa(V) chloride complexes [3]. While thermodynamic studies have predicted the likely chemical forms of these complexes, they remain controversial, and their structural details have remained elusive until now [4].

We identified two distinct structures of Pa(V)-chloride complexes at 3M and 12 M HCl using EXAFS analysis. Additionally, the EXAFS spectra adjustments with structures obtained from theoretical calculations reveal a Pa-O bond length of approximately 1.83 Å for the first time, aligning more closely with theoretical predictions [1-3]. This finding confirms the persistence of an oxo bond in Pa(V) chloride systems, advancing our understanding of protactinium chemistry. These results not only reconcile experimental observations with theoretical predictions but also provide a foundation for future investigations into the coordination chemistry of Pa(V).

**Acknowledgements.**

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**Journées Scientifiques 2025**

# UNUSUAL CIRCULARLY POLARIZED LUMINESCENCE APPLICATIONS OF F-ELEMENTS

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Lanthanide-coordination complexes exhibit fascinating optical and chiroptical properties, due to the 4f-4f transitions leading to applications in various fields in materials science or biology. In particular magneto-(chir)optical correlations and emerging circularly polarized luminescence applications in bioimaging.

In this contribution, we reported unusual chiroptical properties of 4f but also 5f elements like the induction of Circularly Polarized Luminescence of an achiral Eu(III) Complexes via interaction with the NikA Protein and the generalization of CPL properties to Actinides derivatives like Cm(III) complexes.

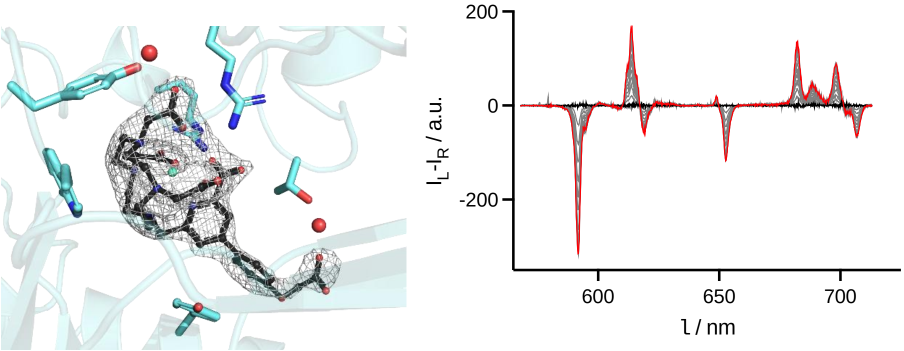

**Figure :** Supramolecular interaction eu Eu(III) cyclen complex with NiKA and related CPL titration.

**Acknowledgements.** We thank The groups of Drs. B. Le Guennic, F. Pointillart, O. Cador (Univ Rennes) and Pr S. Guy, Drs. B. Baguenard and A. Bensalah-Ledoux (ILM Univ Lyon), O.Sénèque (CEA Grenoble) and G.Ung (USA) for fruitful collaboration. We also thank ANR SMMCPL for financial support.

**Journées Scientifiques 2025**

# DESIGN LANTHANIDE DIMERIC COMPLEXES BRIDGED BY A NON-AROMATIC $C_9H_9^{3-}$ LIGAND

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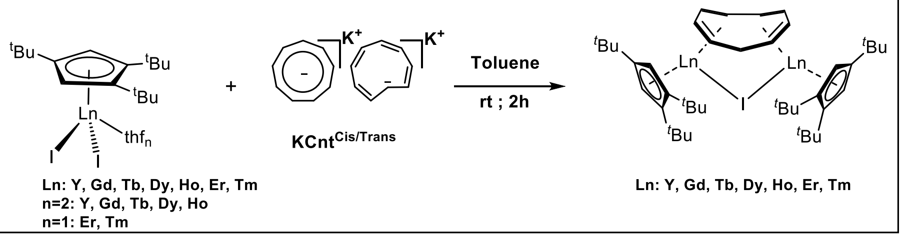
The synthesis of sandwich complexes, wherein f-elements are bonded with functionalized cyclopentadienyl (Cp) and cyclooctatetraenyl (Cot) ligands, has garnered increasing attention due to their distinctive optical,[1] and magnetic properties.[2]

Cyclononatetraenyl (Cnt), a large, mono-anionic aromatic ligand existing as cis/trans isomers,[3] has recently been the subject of extensive research by our group, highlighting its ability to adapt its coordination mode depending on steric hindrance and lanthanide size and to undergo reversible light induced isomerization processes.[4,5]

Under specific reducing conditions, the introduction of a Cnt ligand can lead to the formation of remarkably original and intriguing dimeric complexes. Within these complexes, the ligand appears to behave in a "non-innocent" manner. The ligand appears to be reduced instead of the metal, accommodating two extra electrons and forming a tris-anionic non-aromatic 12л-electron fragment capable of binding two different metal centre. Investigation of such dimeric structures and the unprecedented redox-active behaviour of the Cnt ligand offers exciting avenues for understanding metal-ligand interactions and potentially uncovering novel chemical properties



**Ln: Y, Gd, Tb, Dy, Ho, Er, Tm**
**n=2: Y, Gd, Tb, Dy, Ho**
**n=1: Er, Tm**

**Ln: Y, Gd, Tb, Dy, Ho, Er, Tm**

*Figure 1: General synthesis of dimeric complexes [$Ln_2(Cp^{ttt})_2(Cnt)I$]*

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CenTRA Journées Scientifiques 2025

# ORGANOMETALLIC *F* ELEMENTS COMPLEXES FOR N$_2$ CLEAVAGE AND PHOTOCHEMICAL REACTIVITY

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Organometallic complexes of *f*-elements are an exciting class of organometallic compounds developed in the 1950s. They now concern most rare earth ions in their trivalent and divalent states and many actinides. Such compounds have numerous applications for single electron transfer reactivity and small molecule activation.[1] Due to their optical and magnetic properties, their Single-Molecule-Magnet behavior has impressed with record-blocking temperatures.[2] In addition, highly original magnetic behaviors have highlighted their intriguing binding nature.[3] We will briefly present our methodology for synthesizing organometallic complexes with original geometries,[4] in which the oxidation state is not trivial to assess due to intermediate valent electronic states.[5] Among many large aromatic ligands, the cyclonatetraenyl anion (Cnt), a nine-membered ring, has shown interesting photochemical isomerization and switching properties.[6] Our tribulations will be presented during this conference.

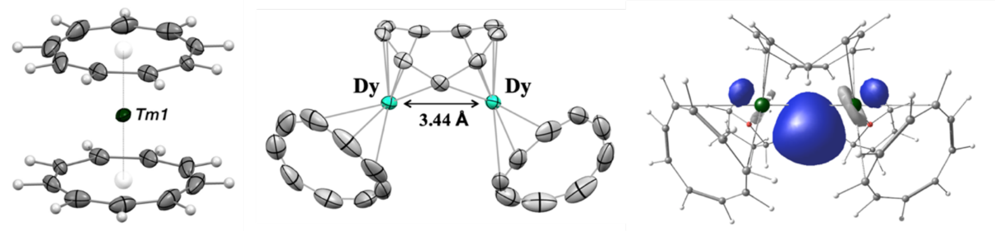

**Figure 1.** Linear thulium complex with the cyclononatetraenyl ligand (left), dysprosium complex (two THF molecules have been removed for clarity) with a possible metal-metal interaction (ORTEP, center, and HOMO, right).

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**Journées Scientifiques 2025**

# CONTROL OF 4F COMPLEXES LUMINESCENCE WITH ORGANIC PHOTOCHROMIC UNITS

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Lanthanide complexes are have unique photophysical properties, including long-lived excited states and narrow bandwidth emission bands. They are also highly versatile tools in various applications, including anticounterfeiting, bioimaging, and information encryption due to the ease in choosing the appropriate emission wavelength from the visible to the NIR range. The optical response of a diarylethene (DAE) moiety can be tailored through isomerisation, providing a means to modulate lanthanide(III) emission with light and to advance further the above mentioned applications.[1] Our group specialises in the photoswitching of NIR emitters, and we have achieved both good contrast between the ON and OFF states and good fatiguability with various ytterbium(III) complexes.[2] We have also recently developed systems with spontaneous return to the ON state.[3] Both will be discussed in this presentation.

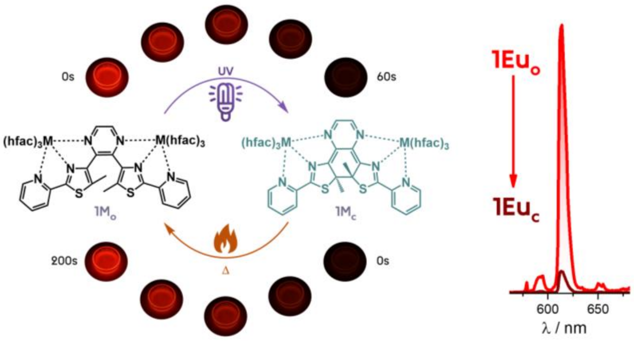

**Figure : Photoswitchable europium(III) complex with spontaneous return to the ON state**

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CenTRA **Journées Scientifiques 2025**

# MULTIMETALLIC ORGANOMETALLIC COMPLEXES OF URANIUM FOR AMMONIA SYNTHESIS

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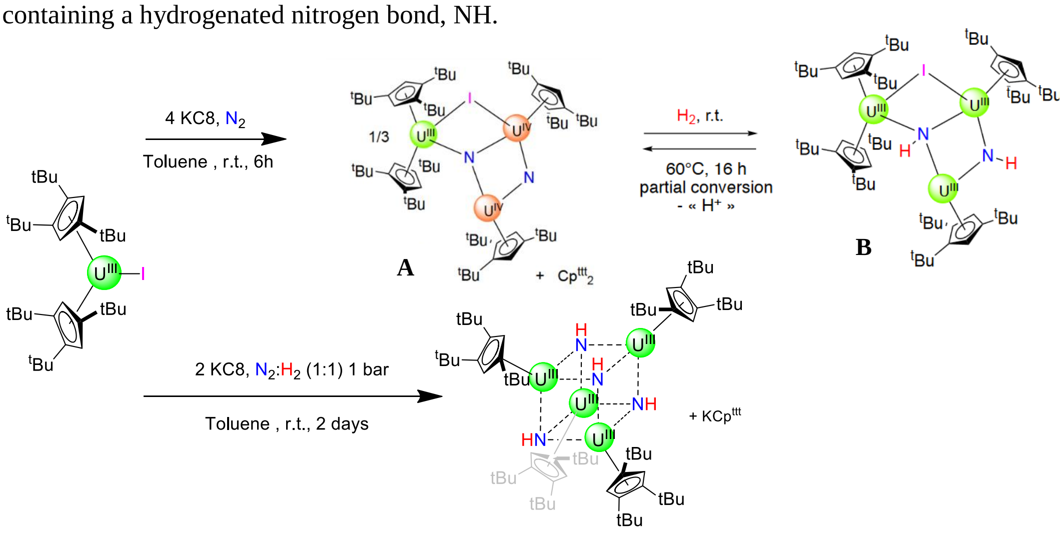
Ammonia synthesis is currently performed using the Haber-Bosch process, which involves the reaction of $H_2$ and atmospheric $N_2$ to form $NH_3$ under catalytic, harsh conditions (450°C, 300 bar). Intensive research is currently conducted to identify alternative pathways to form $NH_3$,[1,2] particularly from organometallic complexes at room temperature.

This project focuses on the behavior of an organometallic complex of uranium (III), $UCp^{ttt}{}_2I$, in the presence of $N_{2(g)}$ and $H_{2(g)}$ to form $NH_3$. Previous works have already highlighted the ability of uranium to fix[3] and activate[4] $N_{2(g)}$, but there are only a few examples of direct hydrogenation of uranium-activated nitrogen[5]. In this work, we propose activating $N_{2(g)}$ with a versatile uranium complex that can fix $N_2$ and subsequently hydrogenate the activated nitrogen. Preliminary results demonstrate the ability of $UCp^{ttt}{}_2I$ complex to coordinate and activate $N_{2(g)}$ under reducing conditions, leading to a nitrogenated cluster (**A**) that can be subsequently hydrogenated (**B**). We are now investigating the reactivity of $UCp^{ttt}{}_2I$ with a 50/50 mixture of $N_{2(g)}$ and $H_{2(g)}$ under reducing conditions, leading to a tetrameric uranium complex (**C**) containing a hydrogenated nitrogen bond, NH.



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# THE IMAGING CRYSTALLOPHORE, FROM PROTEIN CRYSTALS IMAGING TO IN VIVO CRYSTALLIZATION

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Determining the 3D structure of proteins is a crucial step for understanding their biological functions and plays a key role in drug and vaccine design in the pharmaceutical industry [1]. X-Ray crystallography (XRD) remains the technique of choice to achieve accurate structural determination of protein crystal, but despite the recent XRD improvements, only about 15% of isolated proteins reach a complete structure determination, due to three major chokepoints: protein purification, crystal nucleation and phase problem [2]. Therefore, our goal is to tackle simultaneously these bottlenecks by providing direct *in vivo* crystallization. In the past years, our group discovered the *"Crystallophore"*, a lanthanide complex capable of inducing new crystallization conditions and improving crystal diffraction quality for numerous proteins, in addition to its known *f*-element phasing ability [3]. Recently, taking advantage of the luminescence properties of $Ln^{3+}$ complexes, we developed a new family of *''Imaging Crystallophore''*, complexes decorated with specific antennas that provides an easy protein crystal detection exploitable by fluorescent microscopy (one/two photon absorption). Beside the lower nucleating ability of *Im-Xo4* than that of the classical *Xo4*, we demonstrated that a formulation called Mix-*Xo4* composed of *ImXo4*/*Xo4* exhibits a synergy between the imaging properties of the former and the nucleating properties of the latter [4]. In our case, the idea is to use recombinant bacteria *Escherichia Coli* (*E. Coli*) as biological host, inducing the selected protein overexpression and the consequent crystallization in presence of the Crystallophore species to obtain *in vivo* protein crystal, directly ready for next XRD step [5].

**Acknowledgements :** Agence national de la recherche (ANR)

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# LARGE π-LIGANDS FOR THE SYNTHESIS OF BIMETALLIC LANTHANIDE COMPLEXES

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Organometallic complexes furnished with aromatic *π*-ligands have long been of interest since the discovery of Ferrocene in 1951. In relation to the lanthanide and actinides the cyclopentadienyl ($C_5H_5^-$, **Cp$^-$**) and cyclooctatetraenyl ($C_8H_8^-$, **COT$^{2-}$**) ligands, and their derivatives, have proven particularly effective in stabilising a wide array of complexes and facilitating a range of reactivity[1] whilst the coordination chemistry of the larger cyclononatetraenyl ($C_9H_9^-$, **Cnt$^-$**) ligand to lanthanides has recently been explored.[2]

At the same time there has been significant interest in the synthesis of bimetallic complexes and exploiting cooperative effects that may arise from direct or indirect metal-metal interactions.[3] However, this research has largely been confined to the *s*, *p* and *d*-block and there are only limited examples of complexes featuring direct Ln-Ln or An-An bonds.[4–6]

To that end, we are interested in the synthesis of complexes containing large aromatic *π*-ligands which may accommodate two lanthanide ions in close proximity. Herein we explore the suitably of a $C_{10}$ ligand, 1,6-methano[10]annulene, as ligand for metalation with lanthanides.

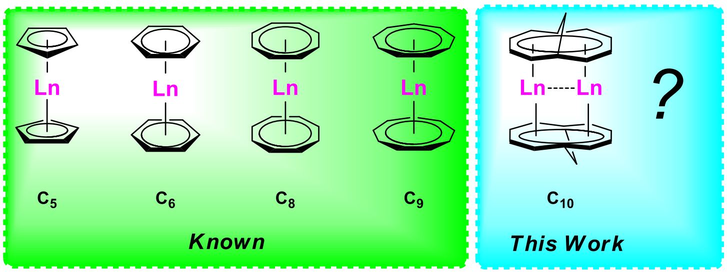

**Figure 1:** Summary of known homoleptic lanthanide sandwich complexes.

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Journées Scientifiques 2025

# CO-DERIVED ETHYNEDIOLATO AS A PLATFORM FOR SMALL MOLECULE FUNCTIONALIZATION

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The transformation of carbon monoxide (CO) into multi-carbon oxygenated frameworks represents a key challenge and opportunity in small-molecule activation, Divalent lanthanide ($Ln^{II}$) complexes are attractive single-electron reductants as their reactivity can be tuned by the nature of both the $Ln^{II}$ metal centre and the ligand.[1] We have shown previously that, using a highly reductive and sterically hindered $Tm^{II}$ complex, selective CO reductive dimerisation is possible, yielding an ethynediolato complex by controlling the stoichiometry of CO.[2]

While ethynediolato complexes are known in f-block chemistry, only rare examples have focussed on their functionalization reactivity.[2][3] In this study, we report two original reactivity pathways of an ethynediolato intermediate generated from a $Tm^{II}$ complex and CO: (1) $CO_2$-induced functionalisation of nucleophiles with possible C–H activation reactivity, and (2) direct functionalisation of the OCCO unit with C=O-based electrophiles, resulting in the formation of novel oxygenated multicarbon products.

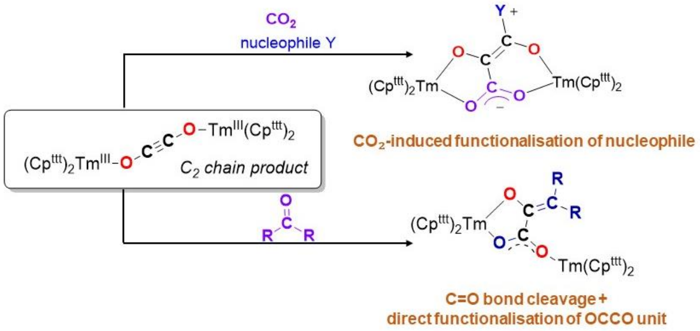

**Figure:** Functionalisation of a OCCO unit with $CO_2$ and C=O based electrophiles.

**Acknowledgement**

We thank the ANR (project number ANR-23-CE07-0012) for funding.

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Journées Scientifiques 2025

# TADF IN LANTHANIDE COMPLEXES: LEVERAGING BOTH ORGANIC AND F-ELEMENT PHOTOPHYSICS

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Rare-earth-containing materials are ubiquitous in diverse applications, with luminescence-based purposes accounting for about a third of their uses.[1] The search for structures with optimal properties for detection, sensing or lighting, for instance, has led to general design rules to optimize luminescence emission in lanthanide complexes, taking advantage of their spectrally sharp and long-lived metal-centered emission.[1,2] In this contribution, we will discuss situations where the complex can undergo reverse energy transfers to an organic chromophore, a scenario that is usually undesired due to its efficiency in deactivating the lanthanide core, but which has been successfully harnessed for thermometry and oxygen detection.[3,4] By tackling the problem from the organic dye standpoint, we will highlight unusual and intriguing photophysical behaviors that lead to new families of TADF (thermally activated delayed fluorescence) emitters. This discovery is expected to open the way for lanthanide-based TADF materials that are well-suited to address current challenges in existing OLED devices.

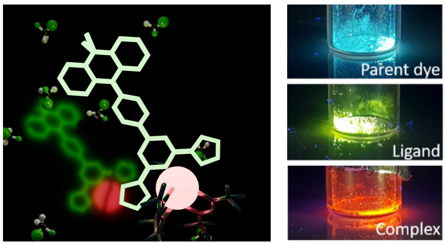

***Figure.** Left: artistic representation of a lanthanide complex.*
*Right: pictures of luminescent powders of TADF dyes under 365 nm irradiation*

**Acknowledgements.** CC thanks the French Ministry of Research and Higher Education and the Doctoral School of Chemistry of Bordeaux for financial support.

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**Journées Scientifiques 2025**

# LANTHANIDE-BASED SUPRAMOLECULAR NANOTUBES AS NEW PLATFORMS FOR OPTICAL AND MAGNETIC NANODEVICES

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Several achievements on lanthanide-based magnetic molecules[1] and in particular Ln-based single-chain magnets (SCM) will be reviewed. We will illustrate how SCM behavior can be observed on lanthanide–radical chains with original topologies such as chiral molecular nanotubes[2] and their derivatives.[3] Then, we will illustrate how metallogels can be formed from these objects while preserving their morphologic and magnetic properties.[4] Moreover, the creation of thick films as well as submonolayer deposits of supramolecular nanotubes on surface will be evidenced.[5] Last, recent findings on enanthiopure gels of nanotubes of SCM and their optical properties will be commented.

**Figure : Supramolecular nanotubes of SCM as solution, gels and surface deposits**

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**Journées Scientifiques 2025**

# SYNTHESIS OF LINEAR DIVALENT SAMAROCENES INVOLVING SPONTANEOUS SM(III)/SM(II) REDUCTION PROCESSES

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The steric and electronic properties of polyarylcyclopentadienyl ligands ($Cp^{Ar}$) have recently led to an increased interest in the synthesis of divalent[1-4] and trivalent[5] f-element complexes bearing these readily modifiable ligands. For divalent lanthanoid complexes, most of the synthetic routes involve a protolysis step of the pro-ligands $C_5Ar_5H$ or $C_5Ar_4H_2$ : (a) starting from isolated divalent or trivalent lanthanoid benzyl species such as $Ln[CH(SiMe_3)C_6H_4\text{-}NMe_2\text{-}o]_2$ or $Ln(CH_2C_6H_4\text{-}NMe_2\text{-}o)_3$,[1,2] or (b) generating in-situ lanthanide aryl species $[Ln(aryl)_2]$ (aryl = Ph, $C_6F_5$) via redox-transmetallation.[3]

We herein report the synthesis of new unsolvated divalent samarocenes with rare parallel $Cp^{Ar}$ ligand arrangements following Harder's approach involving a spontaneous reduction of a Sm(III) species (Figure 1).[1] Furthermore, mechanistic aspects of this intriguing transformation from NMR spectroscopy, XRD analyses and DFT calculations will be presented as well as the limitations of this methodology.

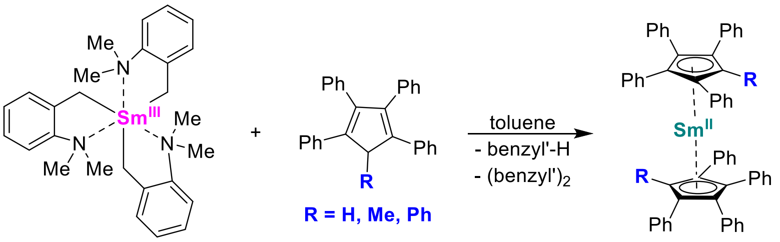

**Figure 1 :** Synthesis of new divalent linear samarocenes bearing polyarylcyclopentadienyl ligands.

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Journées Scientifiques 2025

# EXPERIMENTAL CHARACTERIZATION AND THEORETICAL MODELLING OF X-RAY ABSORPTION SPECTRA OF PROTACTINIUM(V) COMPLEXES

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Protactinium (Z = 91) exhibits unique redox behavior, oscillating between Pa(IV) [1] and Pa(V). In aqueous media, Pa(V) predominates as Pa$^{5+}$ or PaO$^{3+}$, while PaO$_2^+$, common in heavier actinides, has not been observed [2,3]. The presence of a potential mono-oxo bond in Pa(V) can be investigated using X-ray spectroscopies [4].

In February 2024, HERFD-XANES, RIXS, and EXAFS experiments at the MARS beamline (SOLEIL) were performed to study Pa complexes. Unexpected, the spectra of Pa in oxalate and fluoride solutions showed strong similarity (Figure 1) challenging earlier interpretations suggesting mono-oxo formation in oxalic media [5]. To interpret these findings, we employed relativistic TD-DFT [6] and RASSCF [7] simulations at the L$_3$ and M$_4$ edges using EXAFS-derived structural models. These theoretical approaches not only accurately reproduced the experimental spectra but also provided insights into the nature of the electronic transitions.

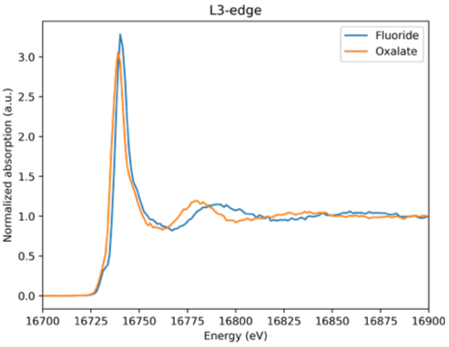

*Figure 1: HERFD-XANES L$_3$ edge spectra of Pa$^{(V)}$ in hydrofluoric and*

This work was supported by ANR (ANR-21-CE29-0027), LABEX CaPPA (ANR-11-LABX-0005-01), and I-SITE ULNE (ANR-16-IDEX-0004 ULNE).

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Journées Scientifiques 2025

# PRO-RADICAL LIGAND-BASED LANTHANIDE COMPLEXES AS MOLECULAR REDOX SWITCHES

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Molecular imaging agents, also known as "intelligent imaging agents," are undergoing significant development due to the urgent need for rapid and effective diagnosis and therapy. Reactive oxygen species (ROS) play a vital role in key physiological processes such as cellular signaling and immune responses. However, their uncontrolled production can lead to oxidative stress, which is thought to contribute to the development of major pathologies, including cancer and neurodegenerative diseases. The design of redox-active probes capable of monitoring oxidative stress or hypoxia in real time holds great potential for the early diagnosis and treatment of such conditions.[1,2] Lanthanide complexes offer unique luminescent and magnetic properties—such as distinctive, long-lived luminescence and paramagnetism—that make them attractive for medical imaging, particularly in optical and magnetic resonance (MR) applications.[1] Nevertheless, their limited capacity for controllable and reversible changes in oxidation state restricts their use as intrinsic redox sensors. Our approach focuses on the design and synthesis of novel pro-radical ligands which, produce an easily detectable change in the complex properties.[3] We herein report the design and synthesis of pro-radical lanthanide complexes containing a redox non-innocent ligand, capable of inducing a response from the coordinated lanthanide ion. The response of these complexes can be exploited in luminescent imaging or CEST imaging.

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Journées Scientifiques 2025

# TOWARDS INNOVATIVE NUCLEAR REACTORS: EXPERIMENTAL DEVELOPMENTS FOR THE CHARACTERIZATION OF CHLORIDE ACTINIDES SALTS

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In the context of climate challenges and the need to diversify low-carbon energy sources, molten salt nuclear reactors (MSRs) emerge as a promising solution. These next-generation systems are distinguished from water pressurized reactor by their high operational flexibility—well suited to the intermittency of renewable energies—and their ability to simultaneously produce electricity and heat for various applications (hydrogen production, industrial processes, etc.) [1]. Furthermore, MSRs presents promising prospects for radioactive waste reduction, notably through the utilization of actinides derived from spent nuclear fuel [2]. In these reactors, the fuel is dissolved in a molten salt mixture that also serves as a heat transfer fluid and confinement medium. Chloride salts, although historically less studied than fluorides, have recently attracted strong interest due to their favorable neutronic behavior at high temperatures and compatibility with industrial processes, including nuclear fuel recycling [3]. These characteristics make chlorides salts suitable for fast-spectrum reactors aimed at efficient actinide utilization and long-term waste minimization. Different chloride actinides salts can be envisaged as fissile or fertile materials: $PuCl_3$, $UCl_3$, $ThCl_4$. That rises the interest for their studies, as well as their analogues, however, their high hygroscopic character requires experimental development for their detailed characterization. Two main techniques form the core of this study: • X-ray Diffraction (XRD), which allows the identification and quantification of crystallized phases present in the mixtures, estimation of overall salt composition, and detection of crystallized impurities • Differential Scanning Calorimetry (DSC), which enables the assessment of salt purity (through melting temperatures), the measurement of fusion enthalpies (related to phase transitions), and heat capacities, which are key data for thermodynamic modeling [4]. The developed protocols consider the radioactive nature, hygroscopicity, and chemical sensitivity of these materials and are conducted under controlled atmosphere conditions with the goal to ensure reliable and reproducible thermodynamic and structural data. This presentation will first focus on the experimental setups developed and showcase the initial findings by DSC study on the $CeCl_3$–$UCl_3$ binary system, providing novel and valuable data crucial for advancing MSR technology.

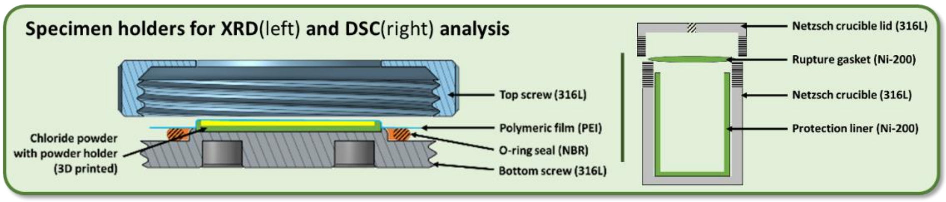

*Figure 1 : XRD and DSC analytical sample holders for actinide chloride salts characterization*

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# CORE EXCITATIONS IN LINEAR AND BENT URANYL COMPLEXES

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X-ray spectroscopies, by their high selectivity and sensitivity to the chemical environment around the atoms probed, provide significant insights into the electronic structures of molecules and materials. For actinide systems, high-resolution fluorescence detected X-ray absoprtion near-edge spectroscopy (HERFD-XANES) at the actinide $M_4$ or $L_3$ edge or at ligand K edges are extensively used obtain information on the actinide and its interactions wirth the local environment [1, 2]. Interpreting experimental results requires reliable theoretical models, accounting for environmental, relativistic, electron correlation, and orbital relaxation effects in a balanced manner.

In this contribution I will discuss our work on employing relativistic electronic structure calculations to devise a protocol to simulate the U $M_4$ or $L_3$ and O K edge spectra in uranyl tetrachloride employing time-dependent density functional theory [3], and established the importance of taking into account equatorial ligands for quantitative agreement with experiment.

This protocol was subsequently employed in a joint theoretical and experimental investigation of the U $M_4$ edge in complexes showing a bent uranyl moiety [4]. Our calculations further underscored the importance of properly describing the interactions with equatorial ligands, and allowed us to rationalize the changes in spectra for the bent uranyl complexes with respect to linear complexes.

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**Journées Scientifiques 2025**

# $H_2$ SPLITTING AND $N_2$ HYDROGENATION INDUCED BY A DIVALENT LUTETIUM COMPLEX

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The direct splitting of $H_2$ and $N_2$ are challenging reactions closely related to the Haber–Bosch ammonia synthesis process. Such reactivity has never been observed for molecular lanthanide species. We show that through careful selection of the ligand scaffold, the isolation and characterization of $[Lu(Cp^{ttt})_2]$ ($Cp^{ttt}$ = tris-(*tert*-butyl)cyclopentadienyl), a rare example of a neutral $Lu^{II}$ complex, is possible.[1]

Compared to the few other $Lu^{II}$ complexes in the literature,[2] $[Lu(Cp^{ttt})_2]$ is kinetically stable but highly reactive as it enables direct $H_2$ splitting at room temperature. This novel reactivity in lanthanide chemistry has been fully corroborated by DFT calculations. In addition, the $Lu^{II}$ complex readily binds $N_2$, leading to an end-on coordinated diazenido $(N_2)^{2-}$ $Lu^{III}$ complex.[3] The latter can be hydrogenated under very smooth conditions to form a unique $Lu^{III}–NH_2$ complex.

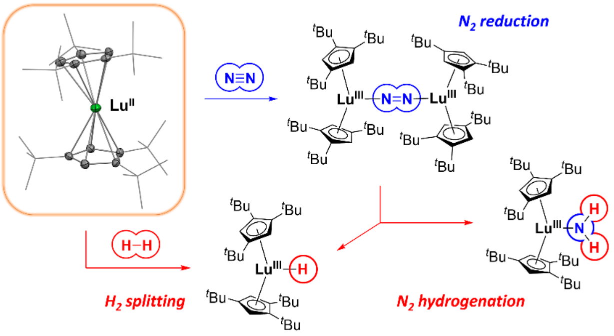

**Figure :** Reactivity of $[Lu(Cp^{ttt})_2]$ towards $H_2$ and $N_2$.

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