



*Review Article*

## Connecting Frontier Research with Industrial Development - Lanthanide and Actinide Chemistry in the European f-Element Network (EUFEN)

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**Abstract.** The chemistry of f-elements, even though often not known to the general public, forms part of many industrial processes, manufacturing and medical applications, such as medical imaging (e.g. MRI scans), strong magnets, data storage media, superconductors, LEDs, catalysis, as well as energy, and metal extraction. It plays a crucial role in the scientific and industrial landscape of the European Union (EU) in fields of energy, security, training, sustainability, and society. The use of these elements widens the scope of synthetic possibilities in chemistry, and materials with outstanding electromagnetic properties have already been realised. The synthesis of lanthanide containing supramolecular materials with exceptional materials properties has already been reported, e.g. the ability to bind and release gases, high-temperature superconductivity, and all-white light emitting diodes. The EUFEN (European f-Element Network) COST action provides cooperative mobility mechanisms for nationally funded f-element chemists pursuing fundamental frontier research to initiate collaborations, training, networking, and dissemination among each other. Novel developments and results in terms of f-element crystal engineering carried out at the University of Malta are therefore part of EUFEN.

to supply industry with trained researchers from universities, restructuring the EU science-base, and thus result in a research output that is greater than the sum of its parts.

Although already more than 200 years old, the chemistry of f-elements (a block of 28 elements at the bottom of the periodic table) can still be considered as one of the areas of chemistry that are least known by the general public. Hardly anybody outside the field of inorganic chemistry will have read or heard of “f-elements” as well as groups of elements called lanthanides, actinides or rare earths; a good example are the actinide elements uranium or plutonium: even though one might know these elements very well in the context of radioactivity or nuclear energy, only a small group of people would know that uranium and plutonium are part of the group of elements in the periodic table called f-elements and that there is a surprisingly rich amount of synthetic chemistry of e.g. uranium and thorium complexes published every year (Bünzli, 2006); a search with the program SciFinder using the key words thorium or uranium complex resulted in over 5000 publications since 2000.

The innocence of the existence of a whole group of 28 elements is somewhat surprising as f-elements (in particular lanthanides) are indispensable components in many materials everybody uses day by day. f-Element chemistry contributes to medical imaging (MRI contrast agents), magnetic (strong magnets), electronic (superconductors), and photonic devices (lasers, phosphors, displays, LEDs), catalysis, energy, and metal extraction and is therefore strategically crucial to science, energy, security, training, sustainability, and society (Blake et al., 1999; Bünzli, 2006; Bünzli & Piguët, 2002; Edelmann, 2009). This wide range of applications is the result of the particular electromagnetic properties of

### 1 Introduction

EUFEN, the European f-Element Network is a COST action which provides cooperative mobility mechanisms for f-element chemists from all over Europe for pursuing fundamental frontier research to initiate collaborations, training, networking, and dissemination with each other (COST, 2014).

Two goals for the action have been identified: (i) to tackle unsolved problems in f-element chemistry and (ii)

f-elements. Often just a very small percentage of f-element (usually between 0.01 and 10%) needs to be present in a material to change its optical, electrical or magnetic properties completely.

The synthesis of lanthanide containing supramolecular materials with exceptional materials properties have been discovered recently, e.g. the ability to bind and release gases, superconductivity, and luminescence (Blake et al., 1999).

In addition to the general lack of knowledge about the existence of these elements in public, there are also a number of ways to name certain groups of f-elements and other related elements in the periodic table. Elements called lanthanides and actinides can either i) be the row of elements from lanthanum (La) to ytterbium (Yb) and actinium (Ac) to nobelium (No) or ii) include also the elements lutetium (Lu) and (Lr) lawrencium, respectively. However, according to the conventions set by the International Union of Pure and Applied Chemistry (IUPAC), the latter (ii) would refer to these groups as lanthanoids and actinoids rather than lanthanides and actinides. Some sources also state that the group of lanthanides consists of the group of elements from cerium (Ce) to lutetium (Lu) (Bünzli, 2006). Rare earths is also an expression which is often used for the group of 4f and 5f-elements. This group consists not only of 4f and 5f elements, but it includes also other elements from Group 3 of the periodic system, namely yttrium (Y) and scandium (Sc).

In view of their large ionic radius and their particular electronic configuration, f-element based research can be extremely challenging from a synthetic point of view. Scientific exchange and collaboration are therefore essential in this field of research. EUFEN offered for the first time a platform for f-element researchers from all over Europe to join forces and tackle the pending questions, such as: What are the principles/mechanisms behind the use of lanthanide complexes as catalysts? How can f-element compounds be treated in computational chemistry and how can we predict the formation of new complex compounds (COST, 2014)?

Due to their special physical and chemical properties, rare earth elements were almost unused and less popular in the field of crystal engineering (Broker, Klingshirn & Rogers, 2002). Novel developments and results in terms of f-element crystal engineering are therefore also an important part of EUFEN.

As EUFEN is the first and only collaborative research network in the field of f-element chemistry, a very large part of the European community of f-element scientists is involved. Over 120 researchers from 24 nations form part of this COST action. Three main working groups were set up (COST, 2014):

a) Synthesis and Structure: the aim is to undertake

the synthesis, structures, and chemical bonding in new f-element compounds, with the scope of discovering novel structures and bonding and rationalising the observed phenomena.

b) Spectroscopy and Computation: the aim is to focus on exploiting existing and new f-element compounds for novel spectroscopic and computational investigations which hitherto have no precedent.

c) Applications: the aim is to explore existing and new chemical bonding and reactivity, or other phenomena, with a view to ultimately delivering research which can benefit EU science, industry, and society as opportunities to exploit new findings become available.

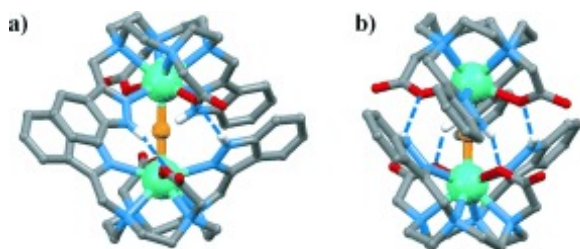
Three different major published outcomes of collaborative EUFEN research will be described below in order to showcase the COST action. Subsequently, our own scientific contribution will be summarised.

## 2 Supramolecular Sensors

One of the most prominent properties of both 4f- and 5f-elements is their large atomic or ionic size. As a consequence their metal ions can usually coordinate to a higher amount of ligands (coordination numbers vary between 7 and 12) than is usually the case for transition metals. The geometries around the f-element centre are less restricted and this makes 4f-element complexes in particular a well-known component in supramolecular chemistry.

Three research participants of EUFEN (Universities of Strasbourg and Bretagne Occidentale, France; University of Coruña, Spain) collaborated on a project which examined the effect of fluoride addition to aqueous solutions of luminescent lanthanide complexes (Ln = Eu, Tb, Yb). (Liu et al., 2014) Upon addition, the formation of a dimeric europium complex **Eu-1** was observed. X-ray crystal structure determination and luminescence spectroscopy revealed not only the geometry of the complexes but also that i) fluoride anions were confined into the cavity that was formed by the two complex molecules and ii) luminescence intensity increased significantly. Synergistic effects of the Eu-F-Eu bridging motif,  $\pi$  stacking interactions, and a four-component hydrogen-bonding network which control the assembly of the two complex molecules around the fluoride ion, are crucial for the above (see Figure 1).

The exact sensing of fluoride in aqueous solutions or solvent mixtures is of great importance for public health (Liu et al., 2014). Fluoride in small quantities can have a positive impact on teeth and bones, whereas higher concentrations of fluoride can result in serious health problems. According to the World Health Organisation the fluoride content in drinking water should be lower than 1.5 ppm (World Health Organization, 2004). However, so far there are just a few procedures known to



**Figure 1:** Crystal structure of the **Eu-1** dimer viewed perpendicular to (a and b) the main pseudo- $C_2$  axis. (Liu et al., 2014)

quantitatively analyse the fluoride content in aqueous solutions.

The authors' new approach is to use the lanthanide complexes described above to sense the fluoride content in aqueous solutions using fluorescence spectroscopy (Liu et al., 2014).

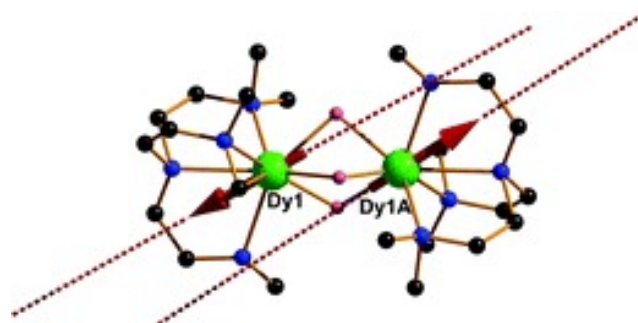
### 3 Single Molecule Magnets

Single-molecule magnets (SMMs) are metal-organic compounds that exhibit paramagnetic behaviour on a molecular level. They can be described as the smallest possible magnetic devices. Potential applications of SMMs are quantum computing, high-density information storage and magnetic memory devices. Lanthanide-SMMs play a leading role in this field of research as the presence of 4f-elements in a complex molecule alters the magnetic behaviour drastically due to the presence of 4f-electrons and thus show a particularly high magnetic moment and single ion anisotropy compared to transition metal SMMs (Christou, Gatteschi, Hendrickson & Sessoli, 2000). However, also systematic research in the field of actinoid (5f) based SMMs emerged in the literature, recently. The outcomes discussed in these papers have resulted from STSMs (Short-Term Scientific Mission) of EUFEN (Liddle, Mills & Wooles, 2010, 2011; Meihaus & Long, 2015; Mougél et al., 2012, 2012).

Okuda (RWTH Aachen, Germany), Layfield (University of Manchester, UK) and coworkers have collaborated within EUFEN and carried out an experimental and ab initio computational study of an asymmetrical, hydride-bridged di-dysprosium single-molecule magnet (Venugopal et al., 2013).

Hydride ligands can be of particular interest for the development of SMMs as they exhibit very strong ligand-field effects. Subsequently, this could have a different effect on the relaxation times in Ln-SMMs compared to metal-organic compounds with oxygen-donor ligands (Luzon & Sessoli, 2012; Rinehart & Long, 2011; Sorace, Benelli & Gatteschi, 2011).

The reported compounds in this study were the first hydride-ligated SMMs. The com-



**Figure 2:** Orientation of the magnetic moments in **Ln-2** (dashed lines). The arrows show the antiferromagnetic coupling. Pink atoms = hydride atoms, blue = N atoms, grey = C atoms (Venugopal et al., 2013).

pounds consist of hydride bridged complexes  $[\text{Ln}(\text{Me}_6\text{trenCH}_2)(\mu\text{-H})_3\text{Ln}(\text{Me}_6\text{tren})][\text{BC6H3}(\text{CF}_3)_2]_2$  **Ln-2**, where Ln = Gd(III), Dy(III) and  $\text{Me}_6\text{tren} = \text{tris}[2\text{-}(\text{dimethylamino})\text{ethyl}]\text{amine}$  (see Figure 2).

### 4 Uranium(VI)–nitride triple bond

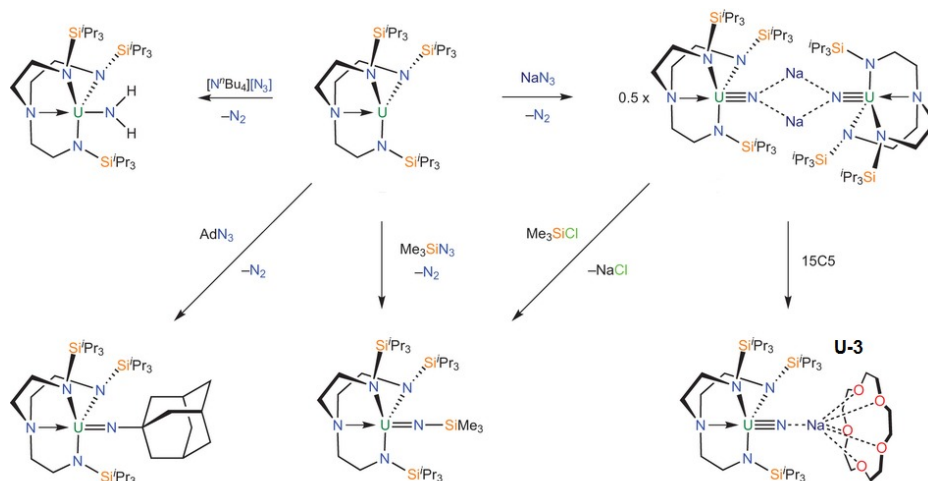
The chemistry of uranium is not only related to its role as a radioactive element, but it is in fact an element well known for its extraordinary coordination chemistry (Bart & Meyer, 2008; Hayton, 2010; King & Liddle, 2014; Lu, 2014; Van Horn & Huang, 2006). Uranium can exist in different oxidation states and can form complexes with high coordination numbers around the actinide (5f) centre due to its large atomic and ionic size.

Whereas the bonding of ligands to 4f elements (lanthanides) is generally known to be mainly ionic, the nature of 5f-element (actinides) ligand bonds is still discussed in recent literature. One of the most controversially analysed aspects of this is the existence of uranium-ligand multiple bonds (Baker, 2012; Bart & Meyer, 2008; Hayton, 2010; King & Liddle, 2014).

During the past years uranium(V)-OR and -NR were reported (R = alkyl group) and thus, the synthesis of a uranium-ligand triple bond was one of the hot topics of EUFEN as it is of fundamental importance to the study of f-orbital participation in metal-ligand multiple bonding (Hayton, 2013).

It was therefore a big break-through when Liddle (University of Nottingham, UK), McInnes (University of Manchester, UK) and coworkers reported the preparation of a complex with a uranium(VI)–nitride triple bond: the terminal uranium(V) nitride complex  $[\text{UN}(\text{TrenTIPS})][\text{Na}(12\text{-crown-4})_2]$  (TrenTIPS =  $[\text{N}(\text{CH}_2\text{CH}_2\text{NSiPr}_3)_3]$  - and  $^i\text{Pr} = \text{isopropyl}$ ) **U-3**. Synthesis was achieved as summarized in Figure 3 (King et al., 2012, 2013).

The existence of a triple bond was proven by single-



**Figure 3:** Reaction scheme for the synthesis of multiple uranium-nitrogen bonds (**U-3**) (King et al., 2013).

crystal X-ray diffraction. The uranium-terminal nitride bond length of 1.825 Å is significantly shorter than the distances reported for uranium amides and uranium amines, which average at around 2.33 Å and 2.66 Å (Lu, 2014).

A thorough understanding of the nature of uranium ligand bonds could result in new developments for nuclear-waste clean-up, as well as new applications in the field of catalysis or in the synthesis of polymeric uranium nitride  $[UN]_n$  for use as a ceramic nuclear fuel (Streit & Ingold, 2005).

## 5 Lanthanide Crystal Engineering in Malta

Solubility is one of the biggest challenges industrial chemistry has to face day by day. Prominent examples are paints, coatings, pigments, and last but not least, pharmaceutically active compounds. Almost all of these compounds are obtained as a solid at some stage during the manufacturing process. Solids are often preferred as the final product because of the obvious advantages in transporting and storing. However, almost all of the above-mentioned products are applied in the form of solutions or suspensions: e.g. drugs are swallowed as a solid and then will have to be dissolved in the stomach to enter the blood stream; paints have to be applied as solutions or suspensions.

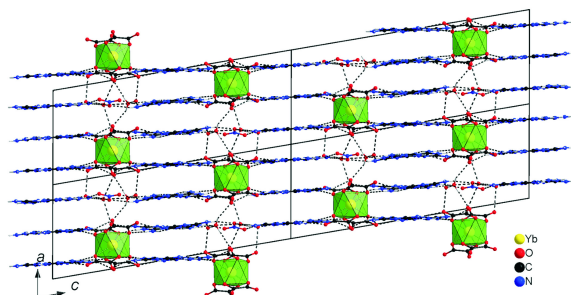
Thus, almost all of the solids produced will have to be dissolved or suspended again when used. The solubility of a solid depends mainly on the amount of attraction between the individual molecules, ions or atoms in the crystal lattice, which again depends on their 3D arrangement. Crystal chemistry of molecular networks, where molecules are linked to each other by non-covalent inter-

actions (H-bonds,  $\pi$ -interactions) or coordinative bonds involving multidentate ligands, can be considered as one of the most promising and appealing branches in modern solid-state chemistry. The formation and recombination of these molecular building blocks permits a unique fine-tuning of the physical-chemical properties of the synthesized compound in the solid-state without altering the actual molecule itself.

During the past decade a new field of science emerged from the above-mentioned necessity to control the arrangement of molecules and ions in crystalline solids: Crystal Engineering. It is “the understanding of the intermolecular interactions in the context of crystal packing and the utilization of such understanding in the design of new solids with desired physical and chemical properties” (Desiraju, 1989). This area of research does not fall neatly within the classical fields of chemistry (organic chemistry, inorganic chemistry, physical chemistry, materials chemistry, biochemistry). It cuts across these traditional vertical subdivisions. Analytical knowledge (e.g. crystallisation techniques, X-ray diffraction, biological processes, and thermo-analytical methods) and the practical experience to synthesise organic, complex, and organometallic compounds are equally important.

In spite of its great potential, very few research groups have applied a crystal engineering approach to molecular metal-based compounds in general (Braga, Grepioni & Maini, 2010; Evans & Lin, 2002; Kanaizuka et al., 2008; Mínguez Espallargas et al., 2010; Zaworotko, 2006). Their inclusion into cocrystal and polymorph screening for the development of the treatment is still to be exploited both from a theoretical and practical point of view.

This is true in particular in the field of 4f-element



**Figure 4:** Crystal structure of **Yb-4** with view along cell axis *b*, dashed lines depict hydrogen bonding (Baisch & Braga, 2009).

chemistry. Lanthanide elements are chemically very similar to alkaline and alkaline earth elements and thus can also influence the solubility of a compound significantly. When surrounded by ligands, these elements have very low toxicity apart from being generally very stable towards oxidation. (Dyson & Sava, 2006; Mewis & Archibald, 2010) They could be utilised effectively not only in the formation of cocrystals or salts to alter the physical properties of drugs, but also to alter crystal growth/solubility of solids which are harmful to the body (e.g. urate crystals). There is currently no precedent literature for this approach.

Our group at the University of Malta functions as a collaborator in all aspects of Crystal Engineering for various 4f-element complexes (ionic and neutral) in the EUFEN COST action. Polymorph screening is carried out in order to explore the existence of new crystal forms with potentially different solubility properties.

The synthesis of lanthanide containing supramolecular compounds with exceptional materials properties has already been achieved as can be seen below (Figure 4) (Baisch & Braga, 2009). This compound has been synthesized by the reaction of melamine with ytterbium oxalate **Yb-4** in boiling water. Single-crystal X-ray analysis of suitable crystals revealed a structure in which melamine forms layers via an extended hydrogen bond network. The lanthanide complex molecules connect these layers vertically by multiple hydrogen bonds.

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