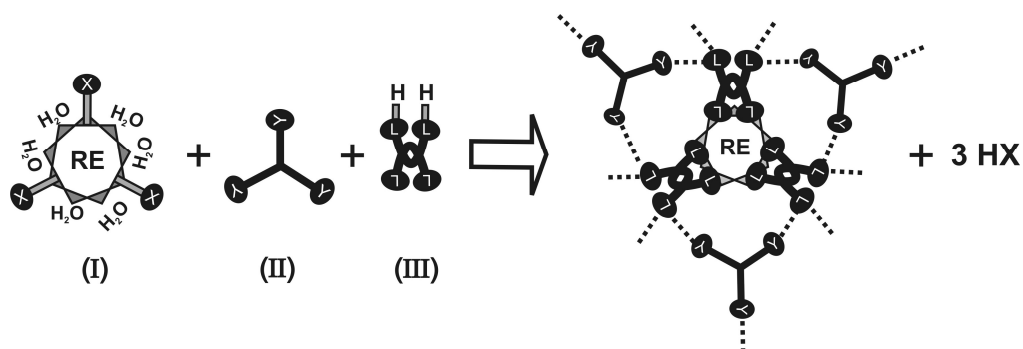


## 1. FINAL PUBLISHABLE SUMMARY REPORT

With “RECrystEng” (Rare Earth Crystal Engineering) we have deployed a new approach for the discovery of crystalline materials with specific optical and magnetic properties, such as fluorescence or magnetic memory. The use of metals from the rare earth series has offered a wide range of materials chemistry in the past, in which compounds with outstanding electromagnetic properties have already been discovered. We have now used rare earth-containing complexes for crystal engineering, the burgeoning field of designed crystalline 3D molecular materials.

An important aspect of this project was to keep the production costs (energy, solvents, special equipment) of the new compounds as low as possible. This Green chemistry approach was successfully applied by using solvent-free solid-solid preparation techniques, such as grinding and liquid-assisted ball-milling. These methods are especially appropriate for high-yield low energy production of the new crystalline rare earth materials.

Complexes of rare earth metals with chelating molecular fragments were used as inorganic building blocks to connect protonated organic molecules (organic tectons) to each other. The ligands have shown both the ability to form inter-molecular interactions and the saturation of only parts of the lanthanide coordination sphere. Scheme 1 outlines the general synthetic approach established as planned in the initial project.

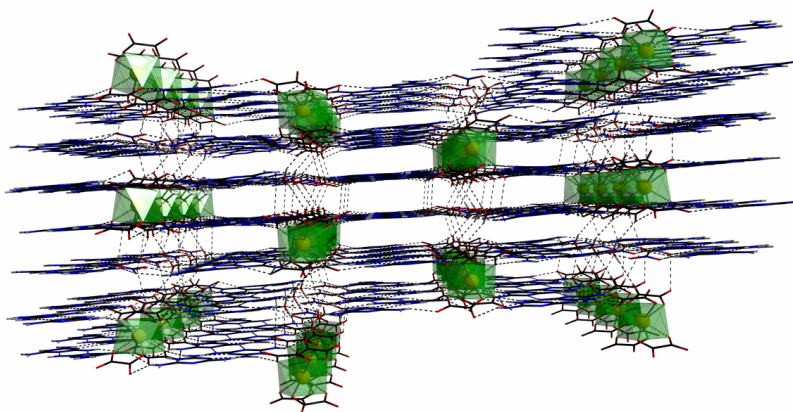


**Scheme 1:** Components and supramolecular tectons for the syntheses of 3D coordination salts; with RE = rare earth ion; X = NO<sub>3</sub><sup>-</sup>, CO<sub>3</sub><sup>2-</sup>; Y<sub>3</sub> = organic tecton; L = saturating chelating ligand.

One of the most significant results was the successful synthesis of a series of new rare earth containing 3D networks by this crystal engineering approach: coordination salts with composition [C<sub>3</sub>H<sub>7</sub>N<sub>6</sub>]<sub>6</sub>[Ln(C<sub>2</sub>O<sub>4</sub>)<sub>4</sub>][NO<sub>3</sub>] (Ln = Eu, Dy, Ho, Yb) and [C<sub>3</sub>H<sub>7</sub>N<sub>6</sub>][Gd(C<sub>2</sub>O<sub>4</sub>)<sub>2</sub>]. Their structure is based on the interaction between the monomeric building-block [Ln(C<sub>2</sub>O<sub>4</sub>)<sub>4</sub>]<sup>5-</sup> or a 2D framework and protonated melamine creating a new motif in lanthanide chemistry. As predicted, some of the compounds showed remarkable electromagnetic properties. Whereas the dysprosium (Dy) derivative showed magnetic memory effects at low temperatures, luminescence measurements of the europium salt revealed strong fluorescence properties with unusually long life times.

The thermal stability, easy availability, and the fact that the synthesis just involves grinding of the solid reagents, transforms this new class of compounds into a potential high-tech material for high-performance rare earth magnets or an essential component in the manufacturing of highly efficient optical fibres or luminescent materials for the transmission of information or light. Thus, these material would enable communication technologies and microelectronics - two of the five major highly competitive sectors marked out in the Commission's communication and proposal for FP7 “Science and technology, the key to Europe's future, (...)” (COM(2005)119).

The structure of the  $[\text{C}_3\text{H}_7\text{N}_6]_6[\text{Ln}(\text{C}_2\text{O}_4)_4][\text{NO}_3]$  salt possesses some remarkable features. To the best of our knowledge, our anion complex molecule  $[\text{Ln}(\text{C}_2\text{O}_4)_4]^{5-}$  is the first example of a fully characterised isolated water-free lanthanide tetraoxalate complex (Fig. 1).



**Fig. 1:** Crystal structure of  $[\text{C}_3\text{H}_7\text{N}_6]_6[\text{Yb}(\text{C}_2\text{O}_4)_4][\text{NO}_3]$  with view on the *ac* plane, dashed lines depict hydrogen bonding.

Furthermore, the organic tectons used for the synthesis of the target compounds often showed a unique combination of hydrogen bonding patterns as well as a rare case of almost perfect coincidence between the crystal structures of a Cu-containing complex and the corresponding compound without the metal.

In this project we have shown melamine to be a “text book” case study of the interplay between molecular shape, hydrogen bonding, and materials property. New crystal structures of the salts of melaminium ions showed surprising hydrogen patterns and will help to gather new insights and conclusions for one of the most important scope of crystal engineering: The understanding of the intermolecular interactions in the context of crystal packing and the utilization of such understanding in the construction of crystalline materials.

### *Conclusion*

“RECrystEng” has led to the successful opening of a new synthetic gateway for a substantial series of rare earth materials with new and potential important electromagnetic and structural features. Our new approach towards the “design” of functional higher dimensional molecular solids and coordination polymers was successful and enabled us to establish Green chemistry into the field of applied supramolecular lanthanide materials chemistry.

Due to its interdisciplinary quality this project brought together a number of fruitful collaborations and future projects joined by scientists and industrial companies with advanced scientific experience and newcomers in different fields of research situated in five countries of the European Union (United Kingdom, Italy, France, Spain). A very competitive network was created, with rich potential to establish a strong position for further research activity after this project, funded and represented by European scientists and the 7<sup>th</sup> European Framework Program.

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