

## Separation of Lanthanides Ions from Mineral Waste with Functionalized Pillar[5]Arenes: Synthesis, Physicochemical Characterization and Molecular Dynamics Studies

**Authors :** Ariesny Vera, Rodrigo Montecinos

**Abstract :** The rare-earth elements (REEs) or rare-earth metals (REMs), correspond to seventeen chemical elements composed by the fifteen lanthanoids, as well as scandium and yttrium. Lanthanoids corresponds to lanthanum and the f-block elements, from cerium to lutetium. Scandium and yttrium are considered rare-earth elements because they have ionic radii similar to the lighter f-block elements. These elements were called rare earths because they are simply more difficult to extract and separate individually than the most metals and, generally, they do not accumulate in minerals, they are rarely found in easily mined ores and are often unfavorably distributed in common ores/minerals. REEs show unique chemical and physical properties, in comparison to the other metals in the periodic table. Nowadays, these physicochemical properties are utilized in a wide range of synthetic, catalytic, electronic, medicinal, and military applications. Because of their applications, the global demand for rare earth metals is becoming progressively more important in the transition to a self-sustaining society and greener economy. However, due to the difficult separation between lanthanoid ions, the high cost and pollution of these processes, the scientists search the development of a method that combines selectivity and quantitative separation of lanthanoids from the leaching liquor, while being more economical and environmentally friendly processes. This motivation has favored the design and development of more efficient and environmentally friendly cation extractors with the incorporation of compounds as ionic liquids, membrane inclusion polymers (PIM) and supramolecular systems. Supramolecular chemistry focuses on the development of host-guest systems, in which a host molecule can recognize and bind a certain guest molecule or ion. Normally, the formation of a host-guest complex involves non-covalent interactions. Additionally, host-guest interactions can be influenced among others effects by the structural nature of host and guests. The different macrocyclic hosts for lanthanoid species that have been studied are crown ethers, cyclodextrins, cucurbiturils, calixarenes and pillararenes. Among all the factors that can influence and affect lanthanoid (III) coordination, perhaps the most basic of them is the systematic control using macrocyclic substituents that promote a selective coordination. In this sense, macrocycles pillar[n]arenes (P[n]As) present a relatively easy functionalization and they have more  $\pi$ -rich cavity than other host molecules. This gives to P[n]As a negative electrostatic potential in the cavity which would be responsible for the selectivity of these compounds towards cations. Furthermore, the cavity size, the linker, and the functional groups of the polar headgroups could be modified in order to control the association of lanthanoid cations. In this sense, different P[n]As systems, specifically derivatives of the pentamer P[5]A functionalized with amide, amine, phosphate and sulfate derivatives, have been designed in terms of experimental synthesis and molecular dynamics, and the interaction between these P[5]As and some lanthanoid ions such as  $\text{La}^{3+}$ ,  $\text{Eu}^{3+}$  and  $\text{Lu}^{3+}$  has been studied by physicochemical characterization by  $^1\text{H-NMR}$ , ITC and fluorescence in the case of  $\text{Eu}^{3+}$  systems. The molecular dynamics study of these systems was developed in hexane as solvent, also taking into account the lanthanoid ions mentioned above, and the respective comparison studies between the different ions.

**Keywords :** lanthanoids, macrocycles, pillar[n]arenes, rare-earth metal extraction, supramolecular chemistry, supramolecular complexes.

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