Interaction of protein-functionalized silica with f-block elements

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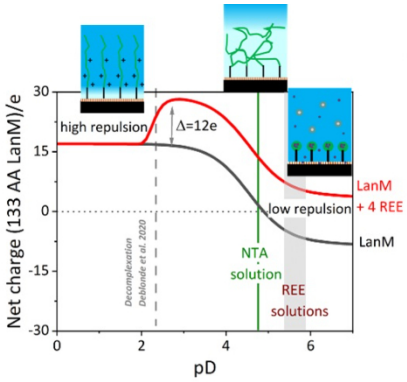
The f-block elements are essential across a wide range of industrial sectors, from advanced high-tech products, batteries, light-emitting diodes, liquid crystals displays, magnets, auto industry, solar panels, wind turbines, electric vehicles, nuclear industry and emerging innovations. As global demand continues to rise and geopolitical tensions intensify, securing self-sufficiency in the supply of these elements has become a critical challenge for the European Union. There is now an urgent need to reduce waste and develop low-energy, cost-effective extraction methods—particularly from industrial by-products.
Recently bioinspired materials have emerged as a promising alternative to conventional extraction methods [1]. Especially, the use of proteins such as the lanmoduline (LanM), a small protein with a mass of 12 kDa and a size of 5 nm (133 amino acids) having a stable disordered structure in complex environments, has shown very interesting extraction properties. In the presence of f-block elements, the protein folds to fit the high-affinity complexation sites required for their retention. This peptide chain folding during complexation drives selectivity: only f-block elements can provide the activation energy required for this folding. In aqueous solution, LanM has picomolar affinities on three complexation sites (from 5 to 35 pM), and a selectivity 5-6 orders of magnitude higher for lanthanides than for classical competing cations such as Ca^{2+}, Cu^{2+} or Zn^{2+}. In addition, this protein releases f-block elements at pH 2 [2].
To prepare functionalized materials for f-block element extraction, we have studied the functionalization of silica surface with this protein and if its functionality was maintained when the protein is grafted, *i.e* if LanM is able to fold and unfold when it complexes and releases f-block elements. To reach this goal, X-ray reflectivity was used to ensure that protein was properly grafted onto the surface of solid quartz substrates. Combined with atomic force microscopy, we were able to determine the arrangement of the immobilized LanM and highlight a surface density around 1 LanM per 5 to 8 nm^2. To go deeper in the behavior of grafted LanM during complexation and release of f-block elements, *in situ* neutron reflectivity analyses were performed on D17 beamline at ILL (Grenoble, France). Several cycles of complexation/ release have been performed with XCl_3 at 10^{-3} M deuterated solutions (X = Nd and Dy). **The results highlighted that grafted LanM keeps its functionality to complex and release f-block element. In addition, we found that the protein's structure varies with pH and that this structuredepends on its effective charge.**

Keywords:
bioinspired materials, surface functionalization, f-block elements, AFM, X-ray and neutron reflectometry



Grafted LanM behavior as a function of pD and of the net charge of the amino-acids present in the LanM filaments (AA).

References:

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