

# Sensitized Eu(III) Luminescence for Probing Ternary Surface Complex Formation

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## 1. Introduction

Migrations of actinides in groundwater is one of the major concerns regarding the underground repository of nuclear wastes. Trivalent actinides including Am(III) are major long-lived radionuclides present in the wastes. It is well-known that chemical interactions of the actinides at the water-solid interface such as minerals and clays are important determinants on the migration rates of the actinides. Naturally abundant humic acids in groundwater can significantly affect to the interactions of actinide with solid phase in a various way including co-adsorption and competitive binding depending on the chemical conditions of the systems [1]. However, the chemical properties of humic acids vary depending on the regions and are not well characterized, resulting in inconsistent results. In order to understand Am(III) adsorption behaviors in the presence of humic acids, we studied a model system of Eu(III), a radio-inactive analogue of Am(III), interacting with silica nanoparticles in the presence of a well-organized small organic ligand, picolinate. Am(III) and Eu(III) share similar chemical behaviors including sorption onto solid phases and thermodynamic properties. Picolinate is bidentate ligand containing carboxylate and a nitrogen donor.

Sensitized Ln(III) luminescence by energy transfer from the bound organic ligands is widely employed in probing metal-ligand interactions [2]. Here, we measured the sensitized Eu(III) luminescence to probe the interactions of Eu(III) at a very low concentration with silica in the presence of picolinate using time-resolved laser fluorescence spectroscopy (TRLFS).

## 2. Results and Discussion

### 2.1 Sensitized Eu(III) luminescence on the silica surface

We observed very strong sensitized Eu(III) luminescence in the presence picolinate either in solution or on surface as shown in Fig. 1, while very weak luminescence was detected in the absence of picolinate at the same experimental condition as shown by the low signal to noise ratio for SiO<sub>2</sub>-Eu. The results show that strongly enhanced sensitized luminescence enables detection of very low concentration of Eu(III), which may not be easy otherwise.

Normalized spectra show that there was no change on the spectral shape of SiO<sub>2</sub>-Eu-Pic luminescence except the enhanced intensity either by addition of picolinate or by increasing the concentration of picolinate. The observations imply that picolinate binds to Eu(III) in the solution phase in a way not to interfere the interactions between Eu(III) and the silica surface.

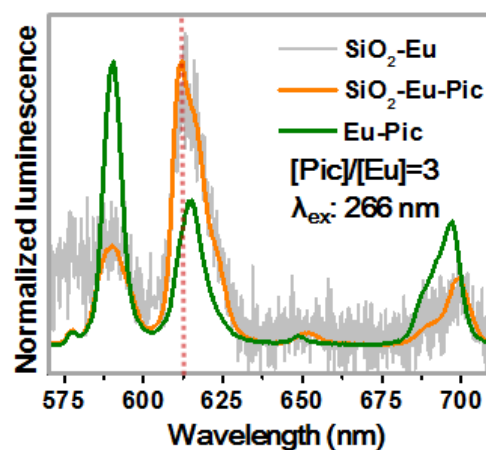


Fig. 1. Normalized sensitized Eu(III) luminescence spectra.

Eu(III) and picolinate concentrations were 6.4  $\mu$ M and 19.2  $\mu$ M, respectively, in 0.1M NaClO<sub>4</sub>, pH 7.2. Silica-Eu samples were prepared by adding 10 times concentrated silica solution (10 mg/mL, pH 7.2) into the Eu(III) solution that pre-equilibrated with picolinate. pH was further adjusted to be pH 7.2. Excitation wavelength of 266 nm (150  $\mu$ J) was used to excite the picolinate and measure the sensitized Eu(III) emission.

## 2.2 Number of inner-sphere coordinated water molecules

We measured the lifetimes ( $1/k_{\text{obs}}$ ) of the Eu(III) species using TRLFS, and calculated the number of inner-sphere coordinated water molecules,  $n(\text{H}_2\text{O})$  according to the equation (1) [3].

$$n(\text{H}_2\text{O}) = 1.05 \cdot k_{\text{obs}} - 0.70 \quad (1)$$

Fig. 2 shows the calculated number of inner-sphere bound water molecules depending on the picolinate concentrations. As increasing the picolinate concentration from 0 to 640  $\mu\text{M}$ , the hydration number continuously decreased from  $\sim 9$  to  $\sim 5$ , indicating formation of the  $\text{Eu-L}_2^+$  complex via a bidentate mode at the 640  $\mu\text{M}$  picolinate concentration. For the case of surface adsorbed Eu(III) in the absence of picolinate, five bound waters indicate that adsorption itself replaces  $\sim 4$  water molecules as reported previously [4]. The presence of picolinate replaced additional water molecule from the Eu(III) on the surface. However, increasing picolinate concentration does not make further changes on the hydration number, in contrast to the case of Eu-picolinate in solution. The results suggest that adsorption of Eu(III) on the silica surface takes place via replacing some parts of interactions of picolinate with Eu(III).

## 3. Conclusions

We studied Eu(III) adsorption on the silica nanoparticles in the presence of picolinate using TRLFS. Strongly enhanced sensitized Eu(III) luminescence enables detection of Eu(III) adsorption on the silica surface as well as Eu(III)-organic ligand complexation at very low concentrations. Our results shows that formation of  $\text{Eu}(\text{picolinate})_2^+$  via a bidentate mode in solution. However, adsorption of Eu(III) on the silica surface can partially replace the picolinate binding interactions and produce ternary complexes of  $\equiv\text{S-Eu-Pic}$ . Further structural studies will be carried out to investigate more details on Eu-picolinate species on the surface.

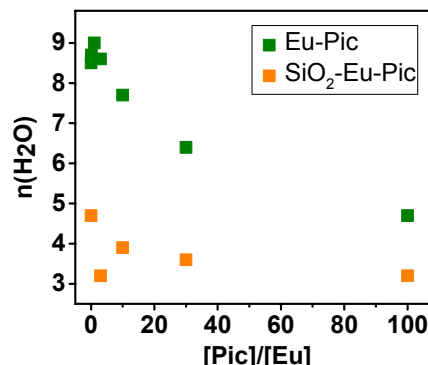


Fig. 2. Number of inner-sphere coordinated  $\text{H}_2\text{O}$  depending on the picolinate concentration. Eu-picolinate complexes (Eu-Pic, green) were prepared at 6.4  $\mu\text{M}$  Eu(III) with various picolinate concentrations in 0.1M  $\text{HClO}_4$ , pH  $\sim 7.2$ . Surface adsorbed Eu(III)-picolinate ( $\text{SiO}_2\text{-Eu-Pic}$ , orange) samples were prepared by adding silica solution (pH 7.2) to the pre-equilibrated Eu-Pic solution and centrifuged at 18000 rpm for 2 hr. The precipitants were resuspended in 0.1M  $\text{HClO}_4$ , pH 7.2. Emission spectra were obtained while stirring the solutions. Excitation wavelength of 266 nm (150  $\mu\text{J}$ ) was used for the sensitized Eu(III) luminescence. Lifetimes were measured by using a gated ICCD with 15-20 ns step delays.

## 4. Acknowledgements

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## 5. References

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