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## Surface-enhanced infrared absorption spectroscopy of lanthanide complexes

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Separation of minor actinides (MA) from lanthanides (Ln) is a key process in the disposal of the radioactive high-level liquid waste from nuclear power plants. MA and Ln ions are practically separated from each other by the solvent extraction with organic ligands, but it is substantially difficult to achieve high selectivity because MA ions such as Am and Cm have similar chemical properties to those of Ln ions. The selectivity of Eu(III)/Am(III) depends highly on donor atoms of ligands; O-donor ligands prefer Eu(III) to Am(III), and S- and N-donor ligands show opposite trends.<sup>[1]</sup> However, the origin of these preferences has not been understood so far from microscopic viewpoints. In this study, we observe IR absorption spectra of Ln complexes by surface-enhanced infrared absorption (SEIRA) spectroscopy to examine the interaction between Ln ions and organic ligands, and finally to understand the relation between the bonding nature and selectivity.

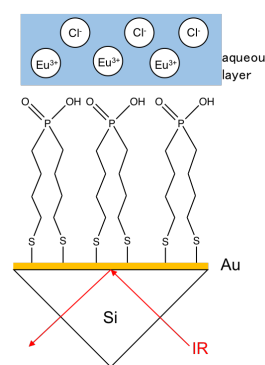


Fig. 1. A schematic drawing of BMPA chemisorbed on a gold surface.

Firstly, we synthesize thiol derivatives of diglycolamide (DGA) and bis(4-mercaptobutyl)phosphinic acid (BMPA), which act as an O-donor ligand. A gold surface is formed by vacuum deposition on a Si prism for ATR-IR measurement. DGA or BMPA is chemisorbed on the Au surface through the Au-S covalent bond (Fig. 1). Aqueous solutions of  $\text{EuCl}_3 \cdot 6\text{H}_2\text{O}$  are put on the surface for the  $\text{Eu}^{3+}$  complexes to be formed, and IR spectra of the complexes are obtained by using an FT-IR spectrometer. We also determine the equilibrium constant for the complex formation by plotting the IR signal intensity as a function of the  $\text{Eu}^{3+}$  concentration in the aqueous solutions.

Fig. 2 displays the IR difference spectra of the  $\text{Eu}^{3+}$ -DGA complex. The spectra show a strong signal at  $\sim 1600 \text{ cm}^{-1}$  and  $\sim 1500 \text{ cm}^{-1}$ , which can be assigned to the C=O and C-O stretching vibrations, respectively. For BMPA, the IR difference spectra of the  $\text{Eu}^{3+}$ -BMPA complex show a strong signal at  $\sim 1050 \text{ cm}^{-1}$ , which can be assigned to the stretching vibration of the  $(\text{POO})^-$  group. These results indicate that the formation of the  $\text{Eu}^{3+}$  complexes can be detected by SEIRA spectroscopy with their vibrational signatures. The equilibrium constant for the complex formation determined with the SEIRA spectra is higher for  $\text{Eu}^{3+}$ -BMPA than for  $\text{Eu}^{3+}$ -DGA. This result is consistent with the trend observed practically in the solvent extraction.

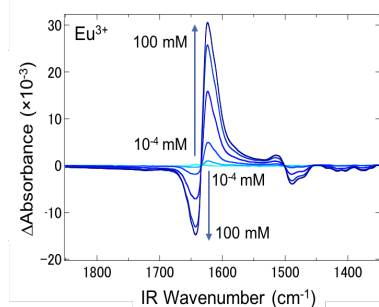


Fig. 2. The IR difference spectra of the  $\text{Eu}^{3+}$ -DGA complex.

[1] Kaneko et al, *Inorg. Chem.*, **54**, 7130 (2015).