

Supporting information for

Spatially resolved Eu(III) environments by chemical microscopy.

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Chemicals

Eu_2O_3 (99.99%), $\text{EuCl}_3 \cdot 6 \text{H}_2\text{O}$ (99.9%) and $\text{Eu}(\text{NO}_3)_3 \cdot 5 \text{H}_2\text{O}$ (99.9%) were purchased from Sigma-Aldrich.

Synthesis of Eu(III) compounds

$\text{Eu}_2(\text{oxalate})_3$ was synthesized from $\text{Eu}(\text{NO}_3)_3 \cdot 5 \text{H}_2\text{O}$ as described by Alexander et al. [1]. Europium phosphate was precipitated from 50 ml of 15 mM EuCl_3 stock solution adjusted to pH 1.5 by addition of solid KH_2PO_4 until precipitation started. Suspension was aged for 1 h before precipitate was removed by centrifugation at 10,000 g. Sodium europium double sulfate ($\text{NaEu}(\text{SO}_4)_2$) was precipitated from 0.1 M EuCl_3 stock solution adjusted to pH 1.5 by addition of solid Na_2SO_4 until precipitation started. Suspension was aged for 1 h before precipitate was removed by centrifugation at 10,000 g. Precipitates were dried before further use at 70°C for 24 h.

Preparation of *Shewanella oneidensis*-MR1 cells and biofilm on calcite

Shewanella oneidensis-MR1 was provided by Thormann Group (University Gießen). Cells were cultured in low nutrient medium described by Davis et al. 2007 [2]. A sample of *Shewanella oneidensis* MR-1 cells incubated with EuCl_3 (50 μM , pH 6, 0.1 M NaCl) for one day, after washing was analyzed by time-resolved laser induced fluorescence spectroscopy (TRLFS) using an excitation wavelength of 394 nm, which is common excitation wavelength for Eu(III).

Ozone cleaned calcite was placed in low nutrient medium freshly inoculated with *S. oneidensis* pre-culture. After incubation for 48 h at room temperature on a shaker (100 rpm) biofilm carrying calcite was placed in EuCl_3 (50 μM , pH 6, 0.1 M NaCl) for 24 h. After gently washing with deionized water to remove salt the *Shewanella* biofilm on calcite was microscopically and spectroscopically investigated regarding distribution of Eu(III) species by luminescence mapping.

Eu(III) transitions relevant for the manuscript

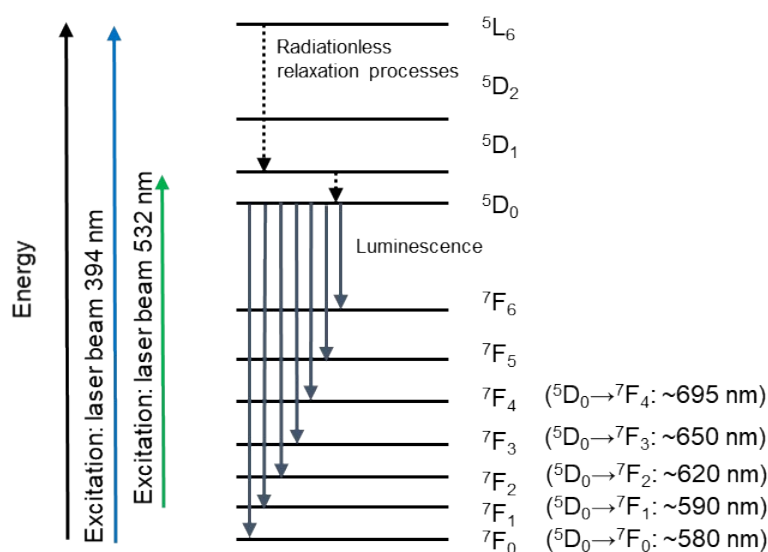


Figure S 1: Part of the energy level scheme of the Eu^{3+} cation including used metal excitation possibilities and luminescence emissions.

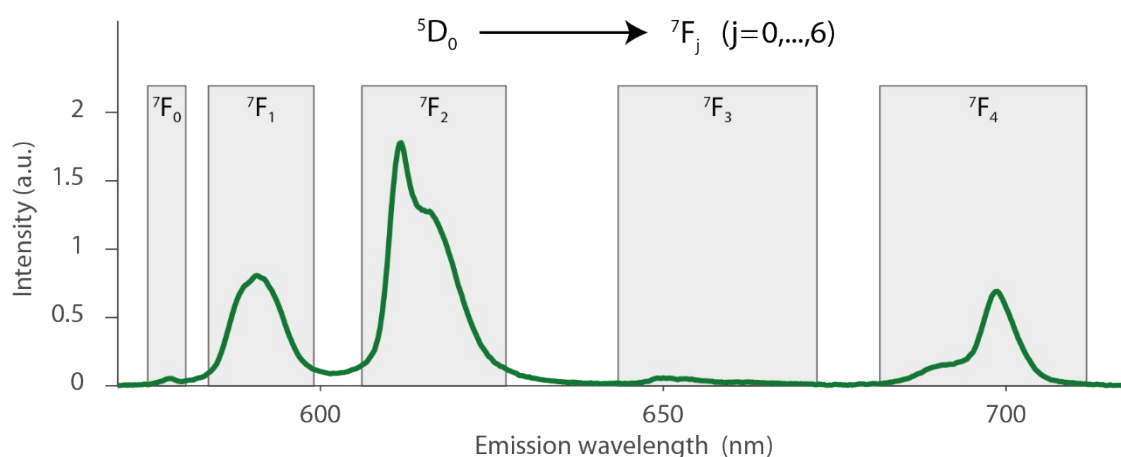


Figure S 2: The emission spectrum of $\text{Eu}(\text{III})$ consists of several electronic transitions. Its main transitions originate from the ${}^5\text{D}_0$ level to the J levels of the ground term ${}^7\text{F}$ with $j=0, \dots, 6$. Often transitions to the ${}^7\text{F}_5$ and ${}^7\text{F}_6$ transitions are not observable. Therefore, the graph shows only transitions up to $j=4$. The ${}^7\text{F}_j$ level can split into a set of crystal field levels. The maximum number of crystal field induced split levels is given by $2j+1$ and depends on the symmetry of the crystal field. This splitting is responsible for the unsymmetrical shape of individual ${}^5\text{D}_0 \rightarrow {}^7\text{F}_j$ transitions.

Luminescence spectroscopic mapping of $\text{Eu}(\text{III})$

Luminescence spectroscopic mapping of $\text{Eu}(\text{III})$ species was carried out with a Raman microscope (LabRAM system, HORIBA Jobin Yvon, Lyon, France) using a 532 nm external Nd-YAG laser (Sacher Lasertechnik, Marburg, Germany) with an output energy of 50 mW as light source. The laser beam is coupled into an Olympus BX-40 microscope (Olympus, Hamburg, Germany). After an optional intensity filter the laser beam was directed through an objective with 10fold or 50fold magnification resulting in laser spot size of ca. 2.6 μm and 0.9 μm , respectively. $\text{Eu}(\text{III})$ luminescence was collected with the same objective and directed through a pinhole (200 μm) to a spectrometer (200 μm entrance slit, 300 l/mm grating) that disperses the light before reaching the Peltier cooled CCD detector (-70 $^\circ\text{C}$). The

sample is fixed on a piezo-electrically driven microscope scanning stage. The analyzed sample areas were pinpointed by using a camera. Acquisition and basic treatment of data was performed with LabSpec 5 software (Horiba Jobin Yvon) and OriginPro 2019.

Time-resolved laser-induced fluorescence spectroscopy of the Eu(III)-RNA system

Ribonucleic acid from torula yeast Type VI was purchased from Merck. The RNA was dialyzed (Slide-A-Lyzer casset, 3.5 kDa MWCO, ThermoFisher) with pure water to remove impurities. RNA (100 mM NaCl, pH 6, 10 μ M EuCl₃) was titrated in 20 steps to a 10 μ M EuCl₃ solution (100 mM NaCl, pH 6) to achieve RNA concentrations of 0 to 74 μ M. TRLFS data were recorded for every concentration. Samples were measured in 2 ml quartz glass cuvettes using an excitation wavelength of 394 nm (Ekspla, NT230, ~5 ns pulse, 1.3 mJ/pulse). The temperature controlled cuvette holder was connected to the spectrograph (Andor, SR-303i-A, 300 l/mm, 100 μ m input slit, center wavelength 640 nm) via a light guide. Spectra were recorded with an ICCD (Andor iStar, DH320T-18U-63, gate width 0.5 ms, linear increasing steps 3+3*x, kinetic series length 21, gain 4000). Data deconvolution was performed with PARAFAC (N-way

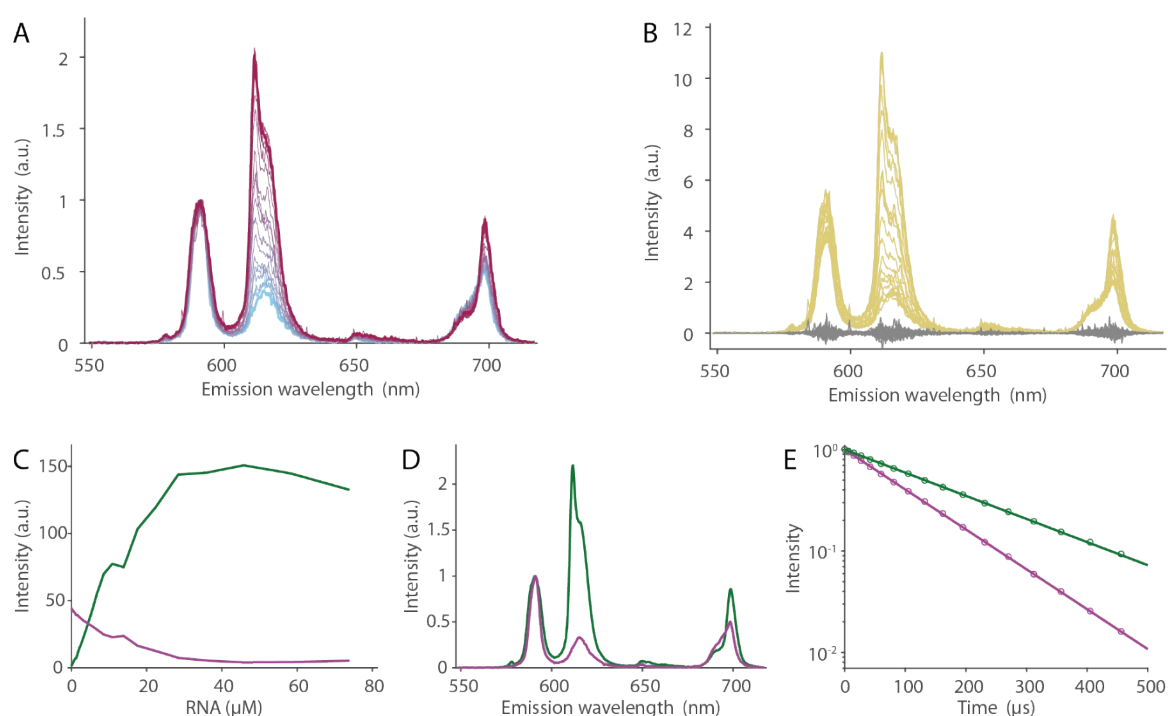


Figure S 3: PARAFAC deconvolution of the TRLFS data of RNA titration to 10 μ M EuCl₃. (A) The t_0 spectra of all 20 samples of the series clearly show changes with increasing RNA concentrations (blue – 0 μ M, red – 74 μ M). (B) Comparison of t_0 raw spectra (yellow) with the corresponding residuals prove the goodness of the used PARAFAC model. (C) The distribution of the two PARAFAC species show the transition from the initial Eu(III)-aquo ion (magenta) to the Eu(III)-RNA complex (green) with increasing RNA concentrations. (D) The species assignment is proven by the emission spectra. The F1/F2 ratio of magenta spectrum is characteristic for the Eu(III)-aquo ion. Changes in this ratio are indicative for Eu(III) complexation. (E) This assignment is further ensured by the luminescence lifetimes ($\tau_{aquo} = 110 \pm 1 \mu$ s, $\tau_{RNA} = 190 \pm 3 \mu$ s). The extended lifetimes of Eu(III)- complexes are usually explained by water molecule displacement from the Eu(III) coordination sphere.

toolbox for Matlab) and is summarized in Figure S 3.

XRD

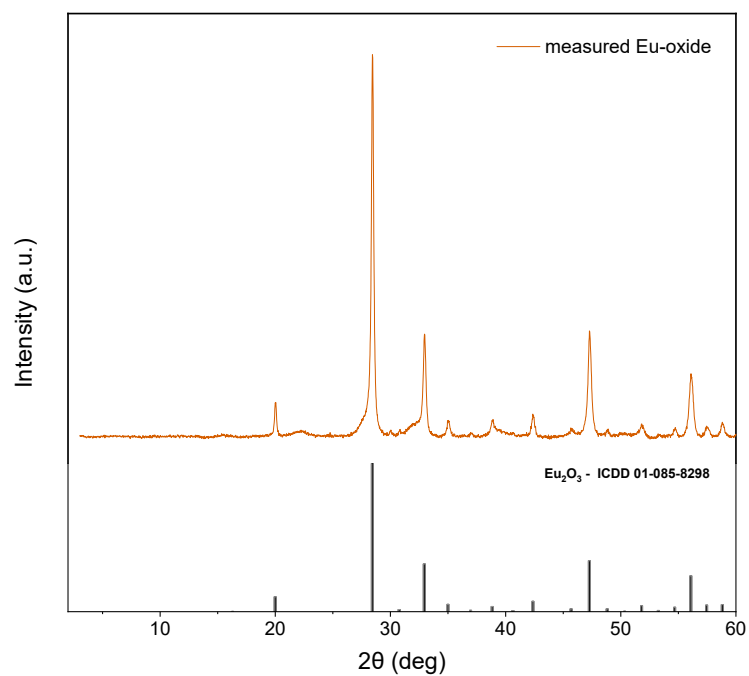


Figure S 4: The powder X-ray diffraction pattern of cubic Eu-oxide (Eu_2O_3).

Powder XRD measurements were performed on a Rigaku MiniFlex 600 diffractometer.

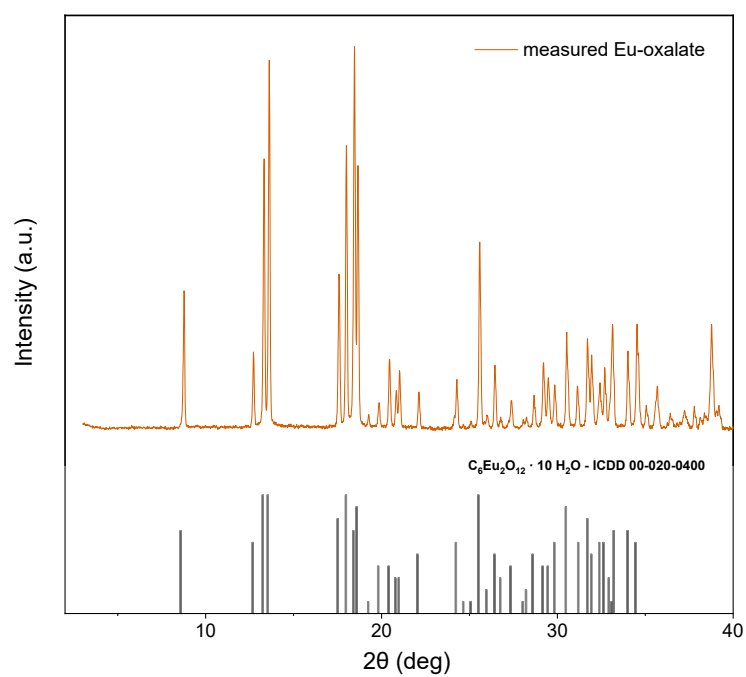


Figure S 5: The powder X-ray diffraction pattern of monoclinic Eu-oxalate ($\text{Eu}_2(\text{C}_2\text{O}_4)_3$).

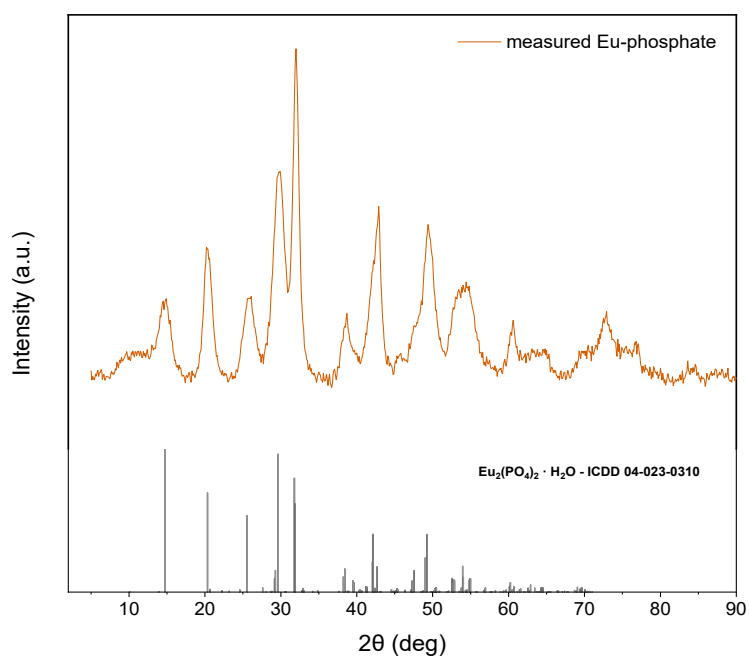


Figure S 6: The powder X-ray diffraction pattern of monoclinic Eu-phosphate (EuPO_4).

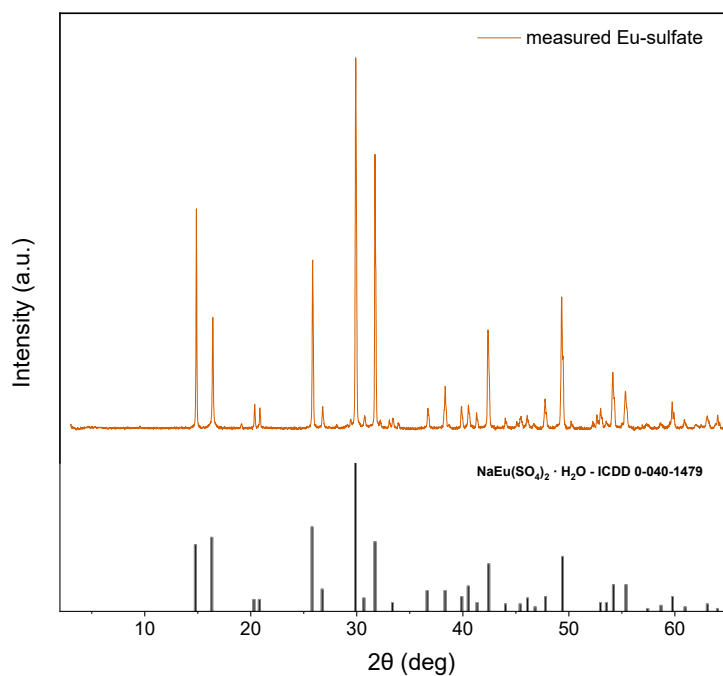


Figure S 7: The powder X-ray diffraction pattern of hexagonal Eu-sulfate ($\text{NaEu}(\text{SO}_4)_2 \cdot x \text{H}_2\text{O}$).