

## Supporting information for

### How tobacco (*Nicotiana tabacum*) BY-2 cells cope with Eu(III) – A microspectroscopic study.

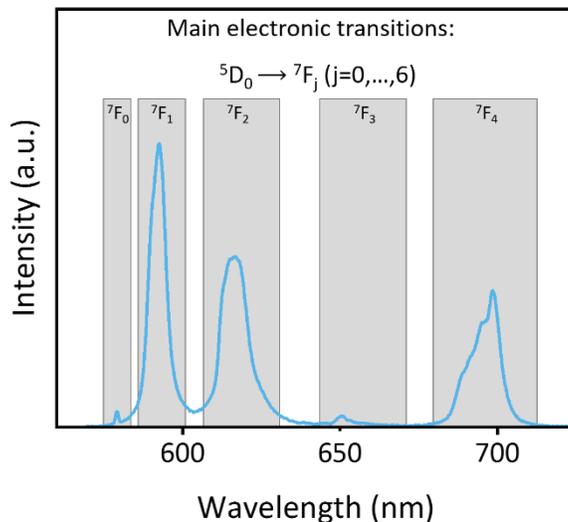
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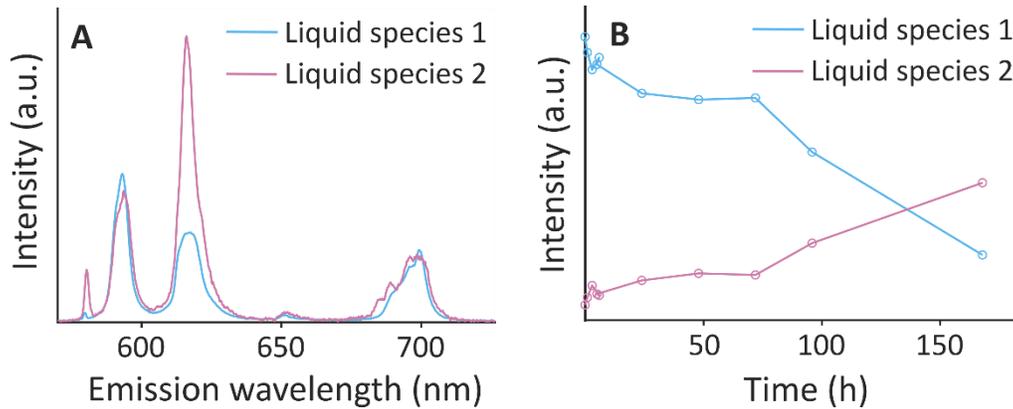
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## Principal Eu(III) luminescence spectra



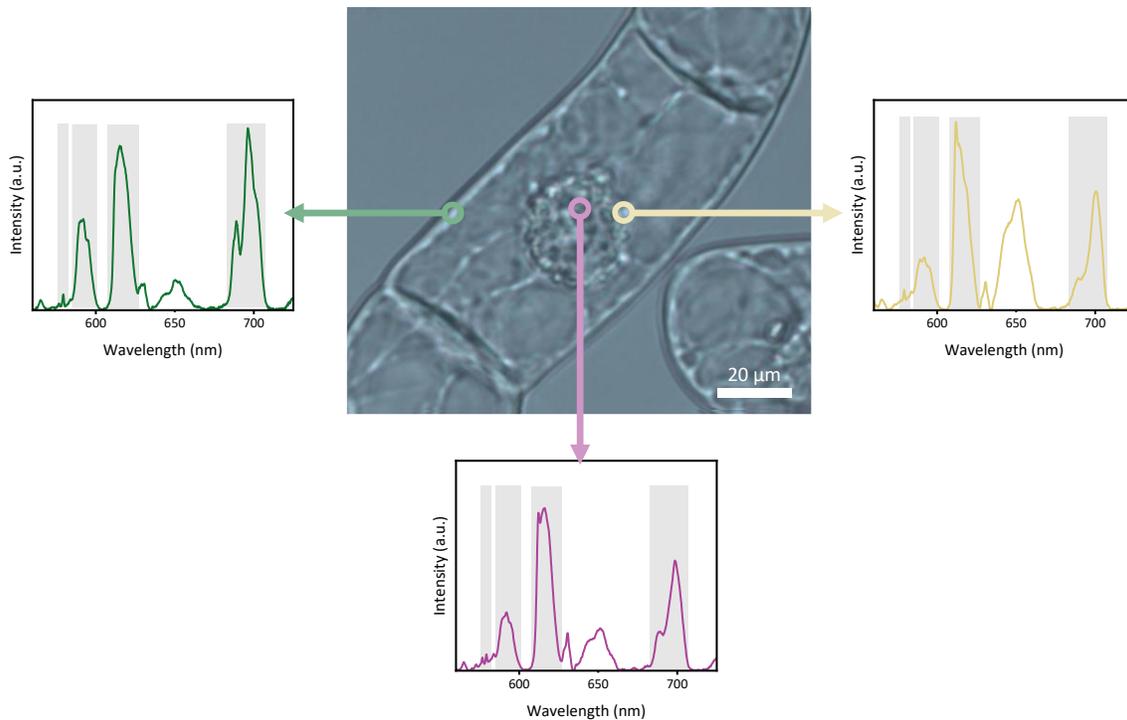
**Fig. S 1:** Example of an emission spectrum of Eu(III). Luminescence emission mainly originates from the  $^5D_0$  excited state to the J levels of the ground term  $^7F_j$  with  $j=0, \dots, 6$ . Often the transitions to the  $^7F_5$  and  $^7F_6$  levels are not observed and hence not shown in here.  $^7F_j$  level can split due to the crystal-field effect into  $2j+1$  sub-levels, depending on the symmetry of the crystal field. Therefore, unsymmetrical shapes of individual emission bands are observed and enable the interpretation of luminescence spectra.

## Eu(III) species in the liquid medium



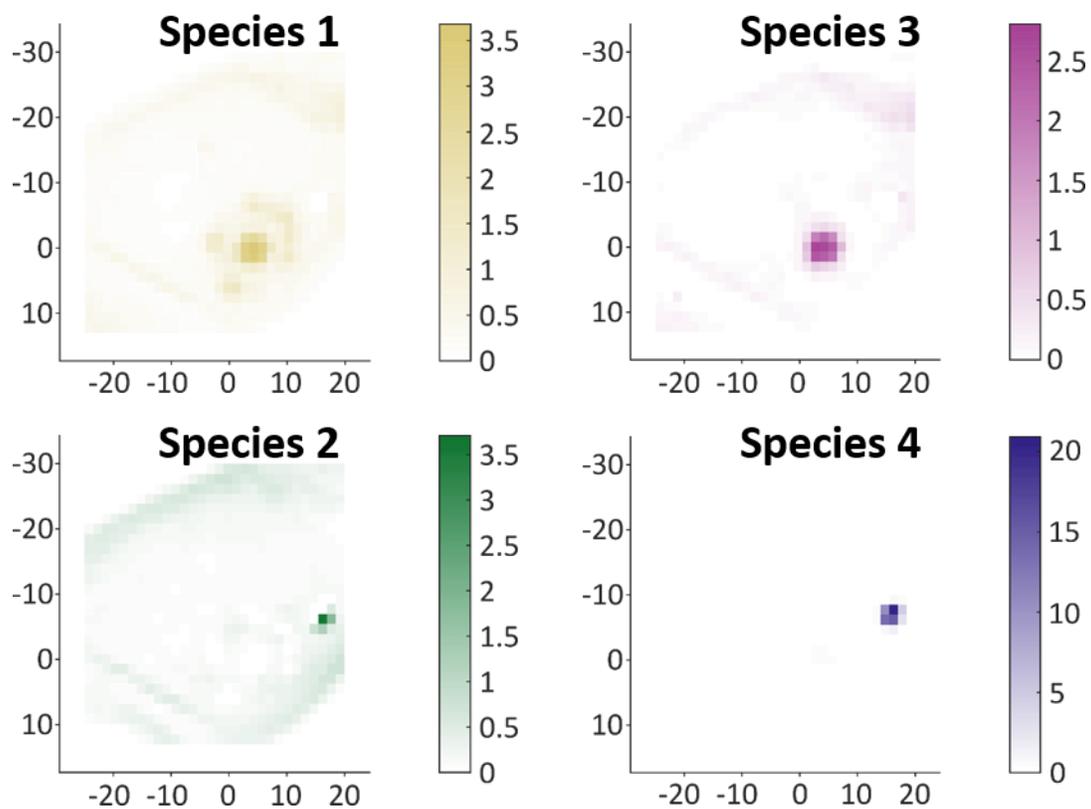
**Fig. S 2:** Deconvolution results from TRFLS data of the time-dependent incubation of BY-2 cells with 100  $\mu\text{M}$  Eu(III), derived from PARAFAC. **A** Normalized single component spectra of Eu(III) species present in the supernatant after separation from the cell pellet, **B** Species distribution in dependence on exposure time. Liquid species 1 represents the bioavailable Eu(III)-aquo ion which dominates Eu(III) luminescence in the supernatant throughout the first 96 h of exposure. The proportion of liquid species 2 increases with time. Considering the medium composition, a Eu(III)-EDTA species can be suspected herein, which is probably a less bioavailable form of Eu(III).

## Point measurements of Eu(III) afflicted tobacco BY-2 cell compartments



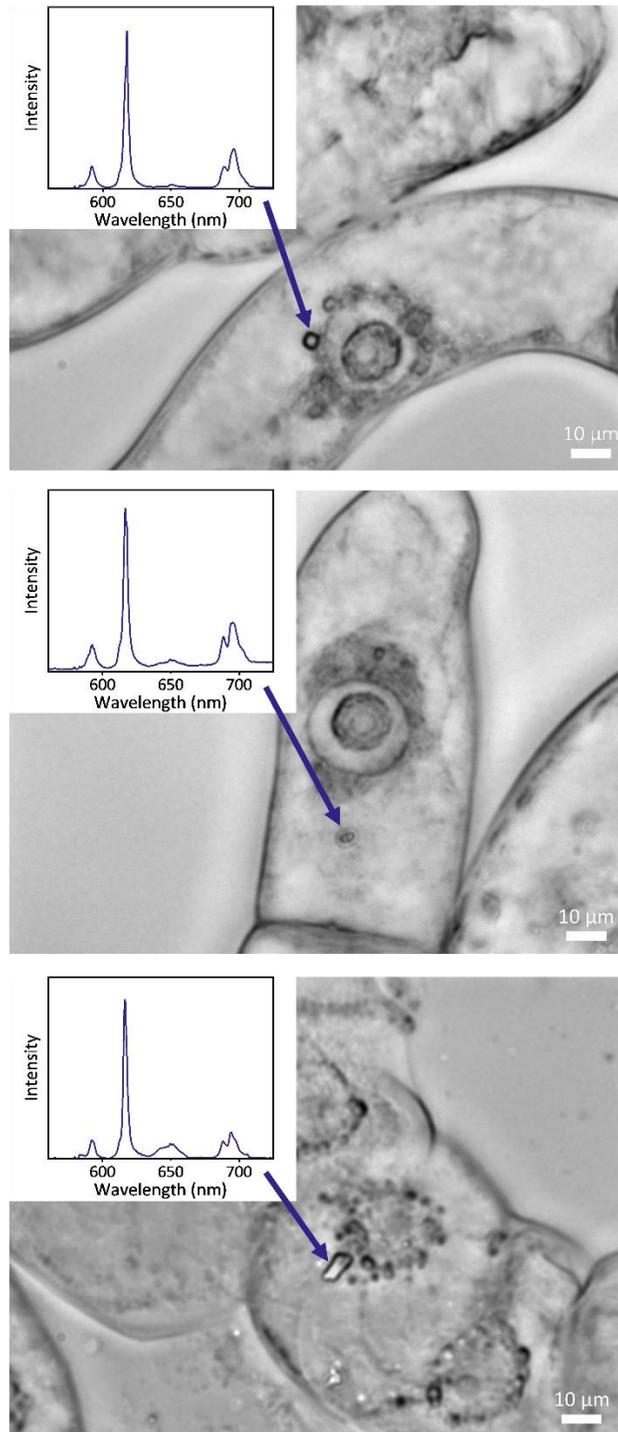
**Fig. S 3:** Raw spectra acquired at different cellular compartments of tobacco BY-2 cells exposed to 100  $\mu\text{M}$  Eu(III) for 24 h. Excitation with 532 nm gives rise to both, Eu(III) luminescence (highlighted in grey) and Raman bands, most remarkably the H-O stretching mode of water at  $\approx 650$  nm. Eu(III) spectra vary in band ratios and band shape due to different coordination of the Eu(III) ion within the cell. For instance, the yellow spectrum resembles phosphatic Eu(III) spectra, whereas the green spectrum likely corresponds to Eu(III)-carboxylate binding environments.

Distribution maps of single Eu(III) luminescence species, derived from deconvolution with NIFA



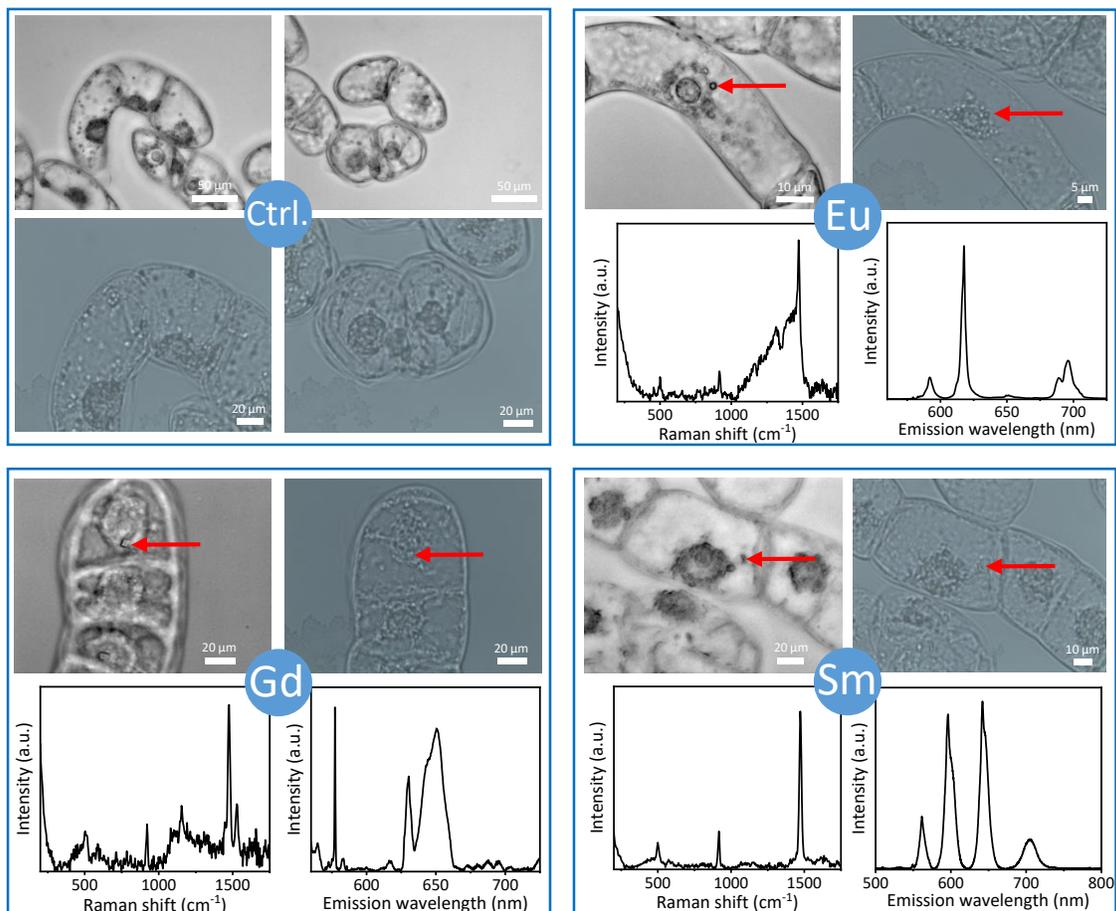
**Fig. S 4:** Distribution maps for single species of Eu(III) in tobacco BY-2 cells, derived from NIFA. Species 1 corresponds to Eu(III) coordinated to organic phosphate groups, e.g. of DNA or RNA. Species 2 likely results from a carboxylate and hydroxyl binding motif. Species 3, with particular occurrence in the nucleolus, is denoted to a protein-bound Eu(III), whereas species 4 is located at the position of the Eu(III)-containing oxalate biomineral.

## Eu(III)-containing oxalate biominerals in tobacco BY-2 cells



**Fig. S 5:** Differential interference contrast microscopy (DIC) images of tobacco BY-2 cells incubated with 100 μM Eu(III) for 48 h and spectra acquired with 532 nm excitation wavelength. Each cell contains one oxalate biomineral that, according to the respective spectrum, comprises of Eu(III). Different morphologies can be seen herein, *e.g.* rectangular, circular and rhomboid. Spectra shown here are not deconvoluted, *i.e.* they comprise of luminescence and Raman bands.

Correlative microscopic and spectroscopic examination of tobacco BY-2 cells subsequent to Ln exposure and control cells without Ln affiliation



**Fig. S 6:** Correlative allocation of Ln oxalate crystals in tobacco BY-2 cells by differential interference contrast microscopy and chemical microscopy with respective Raman and luminescence spectra. For control cells (without Ln), no Raman oxalate signals could be recorded. Bioprecipitates in Eu-, Gd- and Sm-incubated cells show characteristic oxalate Raman signals upon excitation with 633 nm. Additionally, those bioprecipitates in Eu- and Sm-incubated cells exhibit luminescence bands upon excitation with 532 nm and 473 nm, respectively, whereas Gd precipitates only give rise to a Raman water band.