

Room temperature molecular up-conversion in solution with lanthanide self-assemblies

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Here we describe the formation of luminescent supramolecular dimeric capsules selectively sequestering fluoride anions in water and their applications to ion sensing and up-conversion.

The dimers are based on two mononuclear lanthanide complexes $[\text{LnL}(\text{H}_2\text{O})]^+$ which offer a combination of synergistic weak interactions (π - π stacking and hydrogen bonding) promoting the formation of highly stable dimeric self-assemblies $[(\text{ErL})_2\text{F}]^+$ in presence of fluoride ($\log \beta_{2\text{Ln}} = 13.0(3)$, $12.5(1.0)$, $12.6(1.0)$ and $13.0(2)$ for Eu, Tb, Yb and Er, respectively) (Fig. 1).

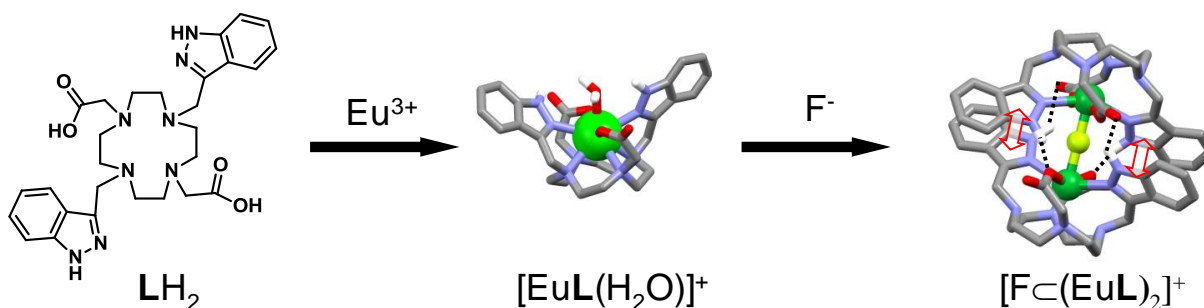


Figure 1. Complexation of Eu^{3+} by ligand **L** and formation of a stable and highly luminescent dimeric supramolecular assembly in the presence of fluoride anions in water.

The principle of fluoride detection is based on the switch ON of the visible emission of the EuL complex, while displacing the water molecule in the coordination sphere (Fig. 1). The EuL complex shows excellent selectivity for F^- in comparison to other halide and a very good sensitivity in aqueous solution (limit of detection < 0.46 ppm).^[1]

These dimeric capsules place the two lanthanide ions in a unique environment: saturated coordination sphere, protection from non-radiative deactivations and very short intermetallic distance ($d(\text{Er} \cdots \text{Er}) = 4.48 \text{ \AA}$), which is favourable to the study of energy transfer between lanthanide excited states. Hence, heterobimetallic Tb-F-Eu dimers have been studied, clearly showing energy transfer from the Tb excited states to the Eu ion in the presence of fluoride. In the case of the homometallic Er-F-Er dimer, room temperature excitation into the Er absorption band at 980 nm in D_2O results in the observation of up-converted emission at 525,

550 and 650 nm attributed to Er centered transitions via two-step excitation.^[2] The formation of the $[(\text{ErL})_2\text{F}]^+$ dimer could be monitored by following the up-conversion emission (Fig. 2).

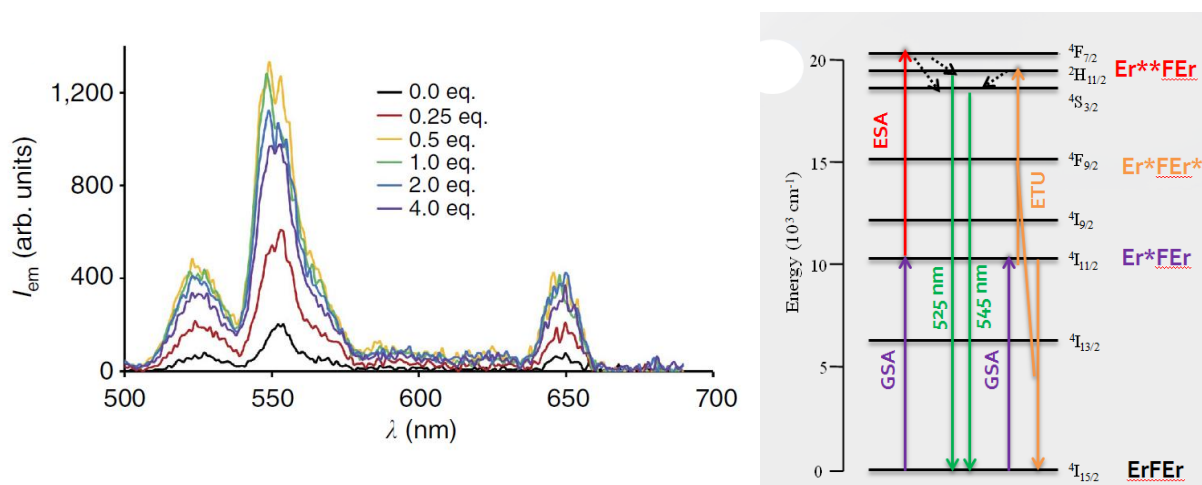


Figure 2. *Left* : UC emission signal of a 1 mM solution of $[\text{ErL}(\text{D}_2\text{O})]^+$ in D_2O ($\lambda_{\text{ex}} = 980 \text{ nm}$) at room temperature, upon addition of NaF. *Right*: Energy level diagram of Er^{3+} .

These results are the first evidence of up-conversion at the molecular level in D_2O and at room temperature. Work in progress is aiming to observe similar properties in non-deuterated water.^[3]

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