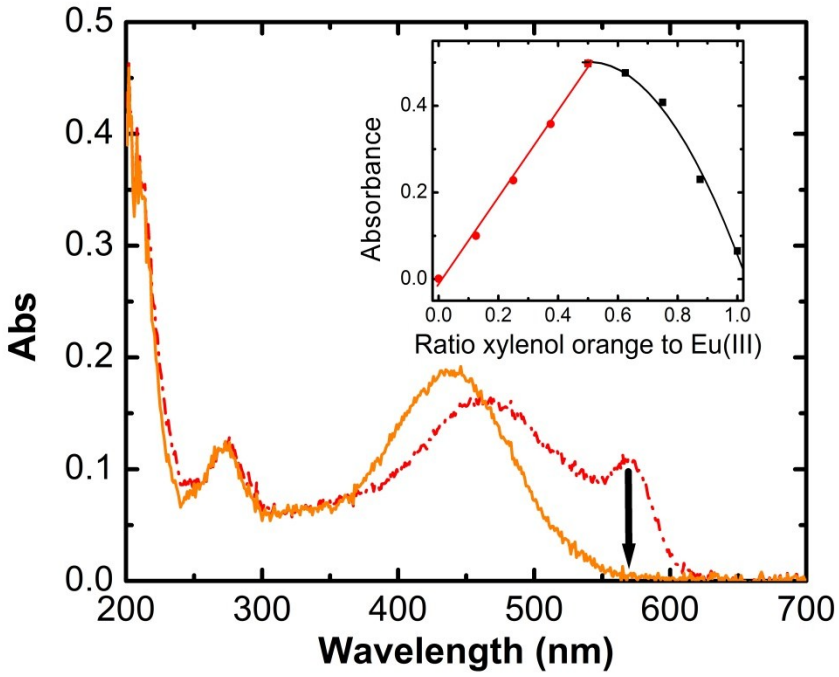
Supplemental information

Metal to dye complex ratio for europium and xylenol orange

Prior to measuring the DTPA-metal ion complexation rate constants individual UV-visible absorption spectra for DTPA, metal ions, and the metal-Xylenol Orange complex were measured. Typical data are shown for Eu(III) in Figure 1. At the concentrations studied, it was found that both free DTPA and metal-complexed DTPA had no measurable absorbance in the UV-Visible absorbance range. It was also seen that the maximum absorption difference between the free dye and the metal-complexed dye occurred at 568 nm.



SI Figure 1. Differences in the absorbance spectra of Xylenol Orange dye (orange solid) and the dye-Eu(III) metal complex (red dashed). Arrow denotes the measured change in absorbance between the dye and dye-metal complex monitored in kinetics experiments. Inset: Determination of the Eu(III) to xylenol orange ratio. From the peak absorbance value (intersection of two fitted lines) a ratio of metal to xylenol orange of 1:1 was calculated.

The stoichiometry of the dye-metal complex was first determined for Eu(III) by plotting the complex absorbance at 568 nm against varying ratios of metal:dye concentrations. From these data (shown in Figure 1, Inset) the stoichiometry was determined to be 1:1 under the conditions studied (pH = 3.6). However, for conditions with excess dye compared to metal, the ratio is not entirely linear, indicating that a higher order complex (such as 1:2) can partly form (equal concentrations and excess metal remained linear and thereby 1:1 complexed), this was

also observed by Kornev *et al.*[29] for samarium. Measured metal-xylenol orange absorption coefficients at 568 nm and these conditions are also listed in Table 1.

SI Table 1. Molar absorption coefficients for M-XO complexes at λ = 568 nm and pH 3.6±0.1.

Metal Ion	10^4 ε ($M^{-1}cm^{-1}$)
Lu(III)	1.12
Er(III)	1.17
Ho(III)	1.16
Tb(III)	1.18
Eu(III)	1.41

In addition to the specific complexation (k_1) and decomplexation (k_{-1}) rate constants for the Xylenol Orange dye we also performed some temperature-dependent measurements for the Lu(III) and Eu(III) reaction with the DTPA-lanthanide-dye system, summarized in Table 2. The measured activation energies were 86 ± 5 and 74 ± 10 kJ mol^{-1} respectively, similar and within experimental error. Additional temperature values for rate constants in the dye-lanthanide-DTPA system are also included in Table 2. The values were determined using pseudo first order approximations after fitting a double exponential function to the original data.

SI Table 2. Complexation (k_1), decomplexation (k_{-1}) and second exponential decay (k_2) rate constants determined for various lanthanide ions with xylenol orange and DTPA. (n.d. – could not be reliably determined).

Metal	Temp. K	$\mathbf{k_1}$ 10^3 $\mathbf{M^{-1}s^{-1}}$	$\mathbf{k_{-1}}$ $\mathbf{s^{-1}}$	$\mathbf{k_2}$ $\mathbf{s^{-1}}$
Lu	288.1	3.50 ± 0.53	6.1 ± 0.5	n.d.
	292.1	5.30 ± 0.85	8.0 ± 0.9	n.d.
	300.3	13.3 ± 0.5	9.0 ± 0.5	n.d.
	303.6	22.4 ± 0.6	9.9 ± 0.4	n.d.
Er	296.2	10.2 ± 0.4	9.2 ± 2.6	0.004 ± 0.002
Ho	296.2	11.6 ± 0.5	12.9 ± 2.9	0.044 ± 0.002
Tb	296.3	28.3 ± 3.4	31.4 ± 2.3	0.87 ± 0.09
Eu	285.2	11.9 ± 3.2	59.0 ± 2.7	n.d.
	290.2	23.8 ± 1.6	95.5 ± 1.5	n.d.
	293.9	26.2 ± 2.5	131.8 ± 1.3	n.d.
	299.2	54.8 ± 6.4	154.0 ± 5.4	7.82 ± 0.34