Table S1. Previously potentiometrically determined stability constant values for Sm and Eu complexes with tda. Overall formation constants are included in the table for each corresponding species.

Ln	Conditions	$[LnL]^{+}$	$[LnL_2]^{-}$	$[Ln(HL)]^{2+}$	[LnL(HL)]	Reference
Sm	0.15 M $NaClO_4$, 37°C	3.455	5.72	6.26		1
Sm	1.00 M $NaClO_4$, 25°C	2.9	4.68	5.59	7.82	2
Eu	6.60 M $NaClO_4$, 25°C	3.54				3
Eu	1.00 M $NaClO_4$, 25°C	2.796	4.17			4

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Table S2. Typical bond distances Ln-S found in structures containing Ln(III) ions and thiol ligands.

Ln	Ligand	Bond distance (Å)	Reference
La	1,4,10,13-tetraoxa-7,16-dithiacyclo-octadecane	3.045	1
La	1,4,10,13-tetraoxa-7,16-dithiacyclo-octadecane	3.031	1
La	1,4,7-trithiacyclononane	3.064	2
La	1,4,7-trithiacyclononane	3.089	2
La	1,4,7-trithiacyclononane	3.126	2
Sm	tda	3.122	3
Dy	tda	3.091	4
Dy	tda	3.099	4
Gd	tda	3.098	4
Ce	tda	3.153	5
Nd	tda	3.148	6
Ce	tda	3.290	7
Ce	tda	3.144	7
Eu	tda	3.1050	8

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Figure S1. Species distribution diagram of the Eu-tda system at 25.0 °C, I = 0.15 mol·L^{-1} $NaClO_4$. Left: [Eu^{3+}] = 1 mM and total [tda] = 1mM. Right: [Eu^{3+}] = 1 mM and total [tda] = 3mM

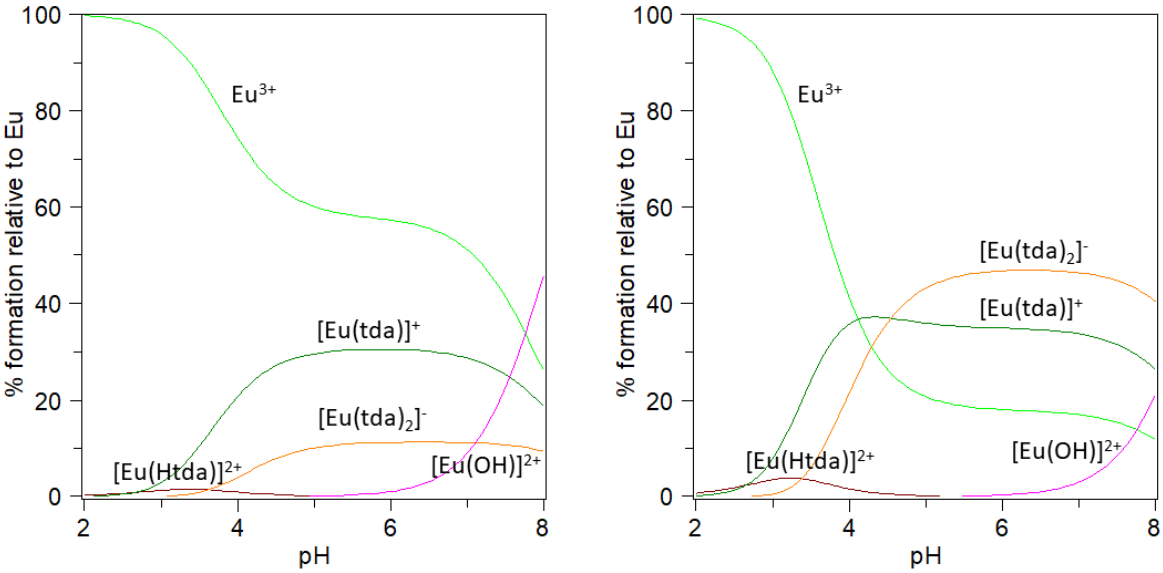

Figure S2. IR spectra of complexes **1** (blue line) and **2** (red line), together with the protonated ligand H_2tda (green line) for comparison.

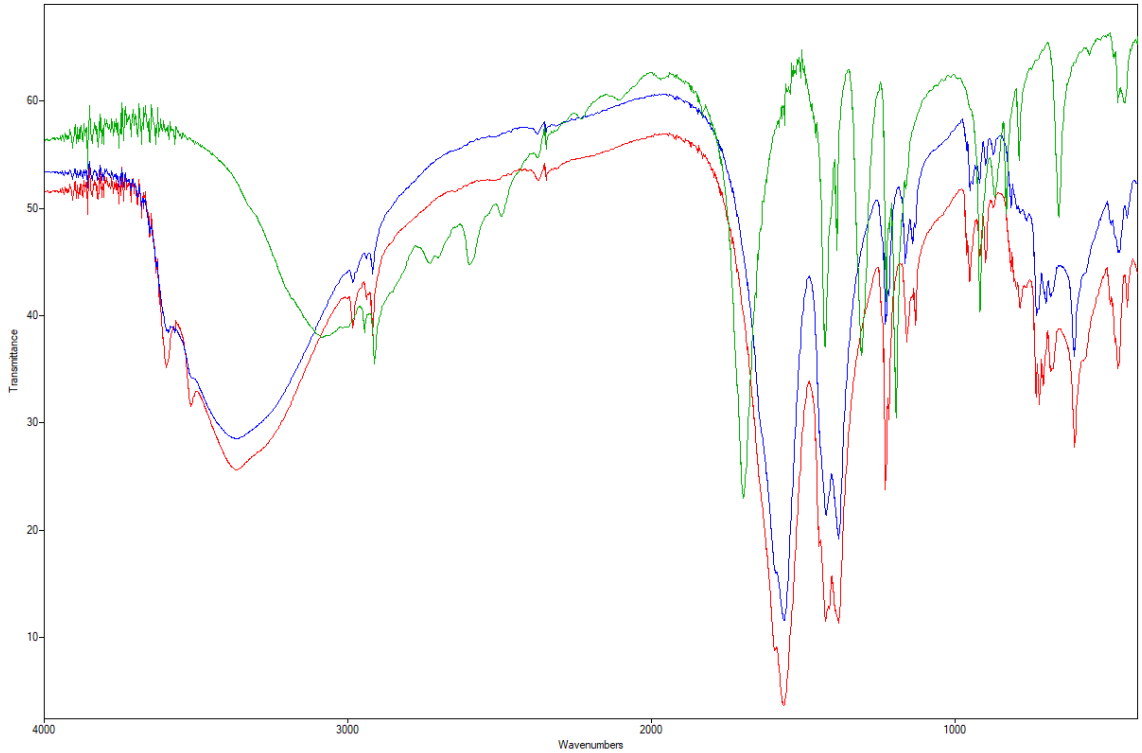

Figure S3. Polyhedra around the Sm(III) ions in **1**. Symmetry codes [i]1-x,-y,1-z; [ii]-x,1-y,-z; [iii]1-x,1-y,-z; [iv]-1+x,+y,+z.

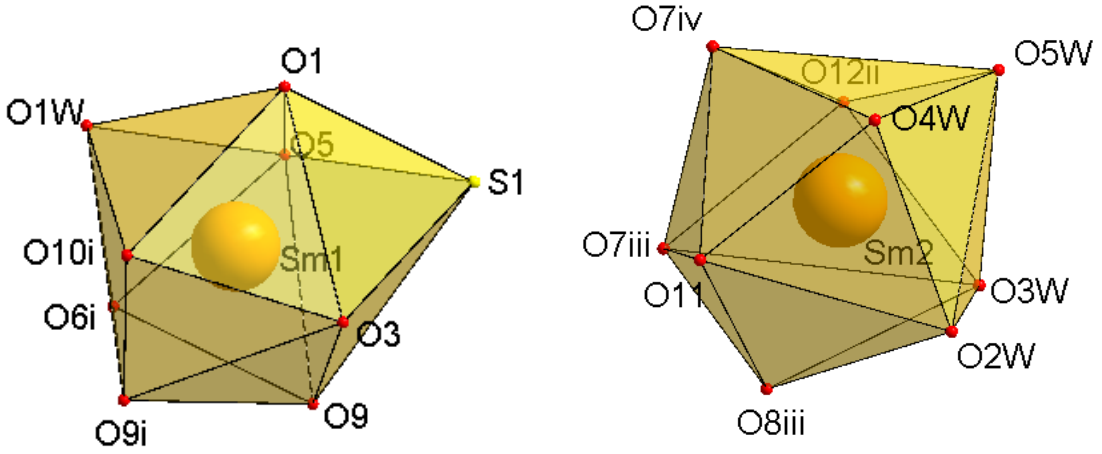

Figure S4. Left: solid-state excitation spectra. Right: emission spectra of compound **1** excited at 392 nm (excitation at 349 nm gave place to a higher baseline that prevented the observation of the Sm emission profile) and using an excitation slit of 10 nm. Transitions assigned to each band are also shown.