Supplementary Information for

Complexation of Cm(III) and Eu(III) with $CyMe_4$-BTPhen and $CyMe_4$-BTBP studied by Time Resolved Laser Fluorescence Spectroscopy

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Emission spectra of the (M(solv.)) and (ML_2) complexes

Cm(III) – $CyMe_4$-BTPhen

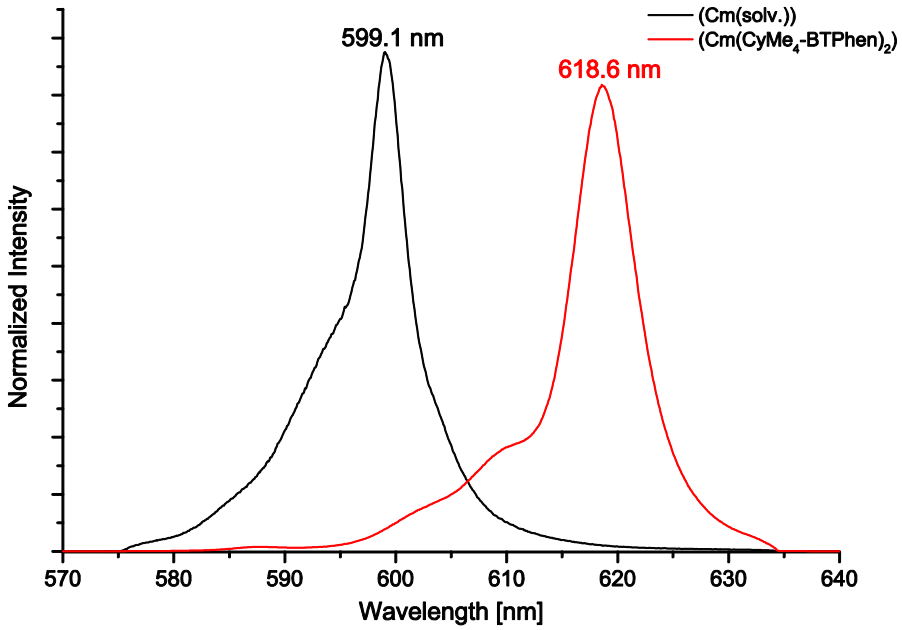

Fig. S1 Normalized fluorescence spectra of the solvated Cm(III) ion and the Cm(III)-$CyMe_4$-BTPhen 1:2 complex in methanol (3.3 mol% water, c($HClO_4$) = 91.2 mM).

Cm(III) – $CyMe_4$-BTBP

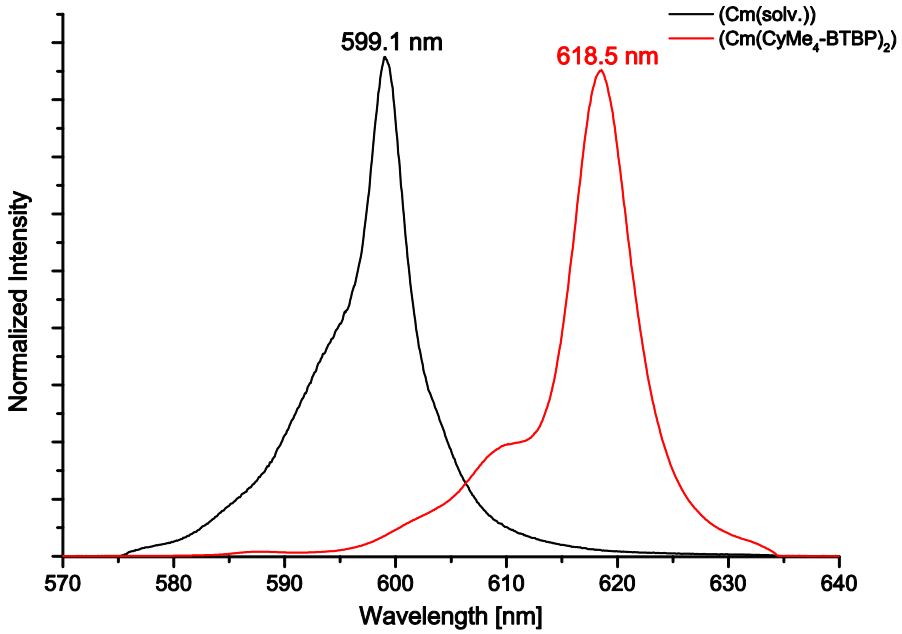

Fig. S2 Normalized fluorescence spectra of the solvated Cm(III) ion and the Cm(III)-$CyMe_4$-BTBP 1:2 complex in methanol (3.3 mol% water, c($HClO_4$) = 91.2 mM).

Eu(III) – CyMe$_4$-BTPhen

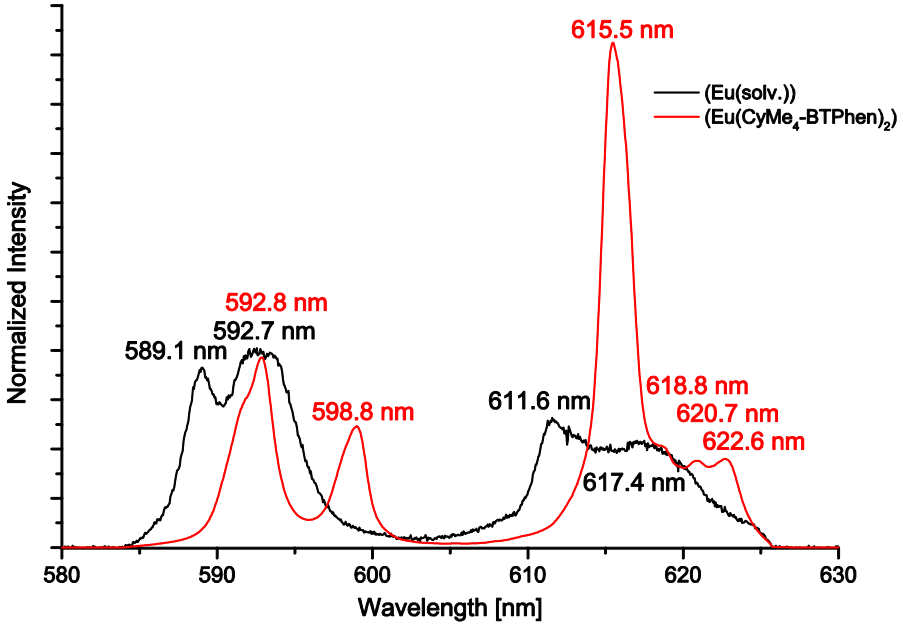

Fig. S3 Normalized fluorescence spectra resulting from the $^5D_0 \rightarrow {}^7F_1$ and $^5D_0 \rightarrow {}^7F_2$ transitions of the solvated Eu(III) ion and the Eu(III)-CyMe$_4$-BTPhen 1:2 complex in methanol (3.3 mol% water, c($HClO_4$) = 91.2 mM).

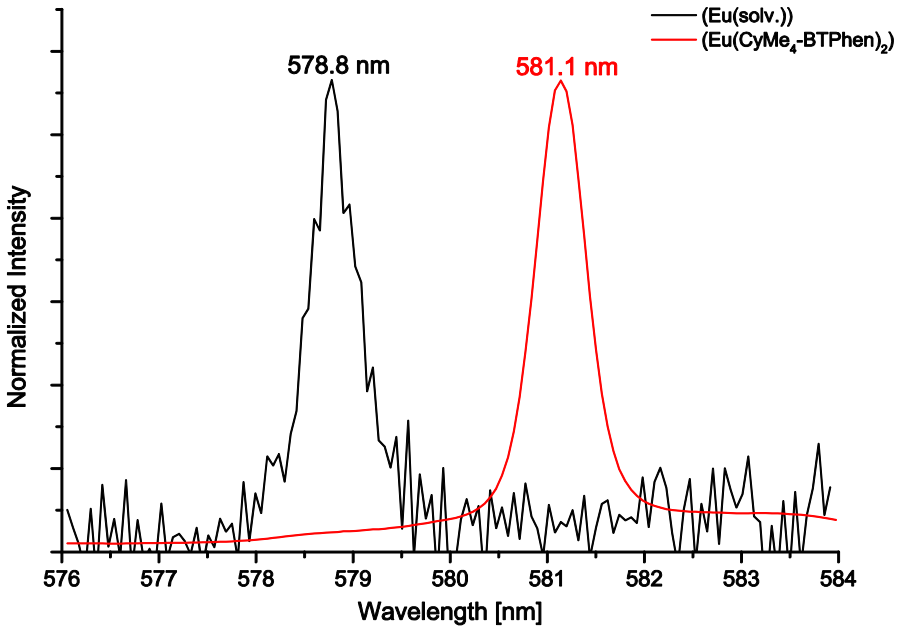

Fig. S4 Normalized fluorescence spectra resulting from the $^5D_0 \rightarrow {}^7F_0$ transition of the solvated Eu(III) ion and the Eu(III)-CyMe$_4$-BTPhen 1:2 complex in methanol (3.3 mol% water, c($HClO_4$) = 91.2 mM).

Eu(III) – CyMe$_4$-BTBP

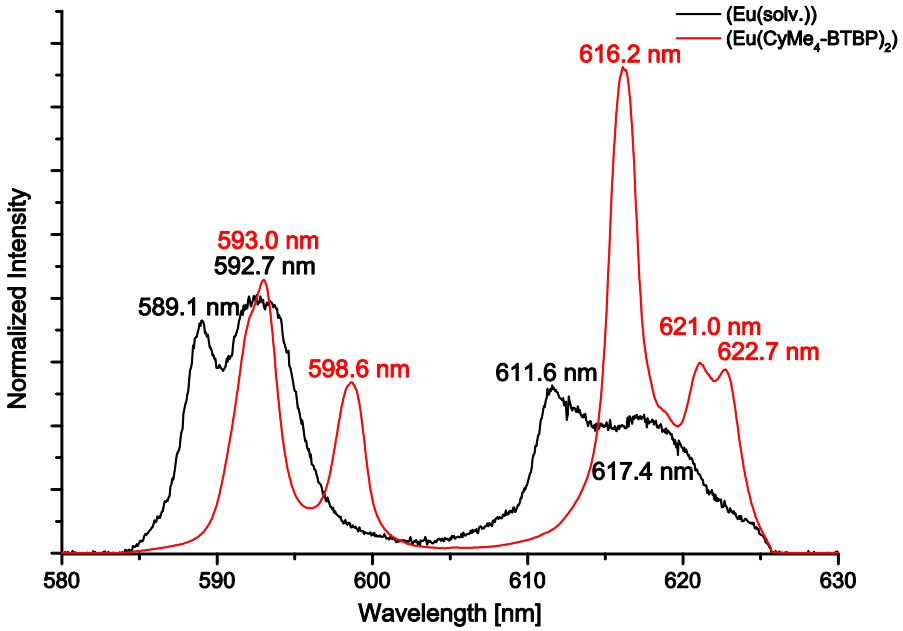

Fig. S5 Normalized fluorescence spectra resulting from the $^5D_0 \rightarrow {}^7F_1$ and $^5D_0 \rightarrow {}^7F_2$ transitions of the solvated Eu(III) ion and the Eu(III)-CyMe$_4$-BTBP 1:2 complex in methanol (3.3 mol% water, c($HClO_4$) = 91.2 mM).

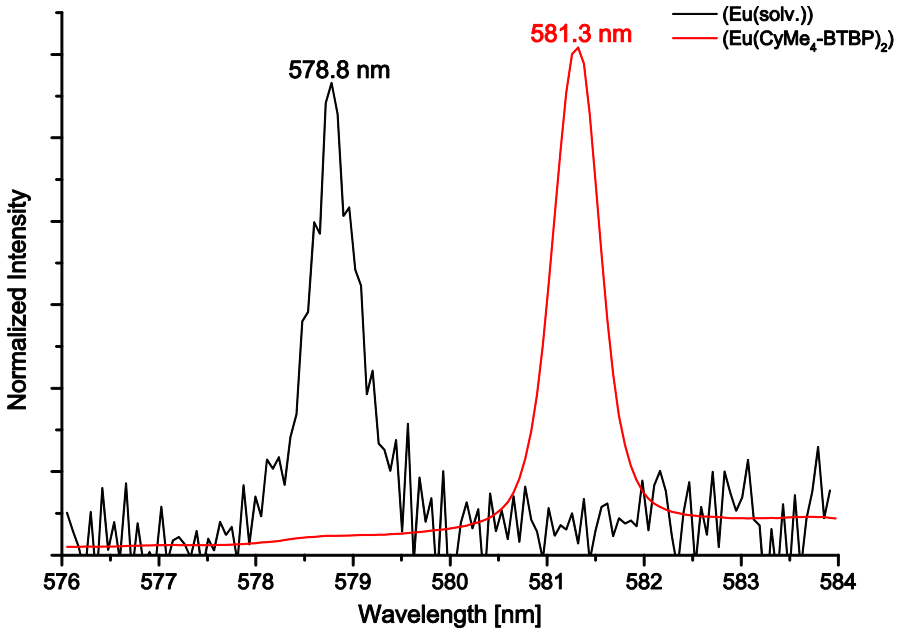

Fig. S6 Normalized fluorescence spectra resulting from the $^5D_0 \rightarrow {}^7F_0$ transition of the solvated Eu(III) ion and the Eu(III)-CyMe$_4$-BTBP 1:2 complex in methanol (3.3 mol% water, c($HClO_4$) = 91.2 mM).

Overview Cm(III) batch experiments

Table S1 Overview of Cm(III) batch experiments performed with $CyMe_4$-BTPhen and $CyMe_4$-BTBP.

experiment name	log β_2	average
Cm-BTPhen 1	13.6	13.8
Cm-BTPhen 2	13.9	
Cm-BTBP 1	12.4	12.4
Cm-BTBP 2	12.4	

Batch experiment Cm(III) – $CyMe_4$-BTBP

Emission spectra

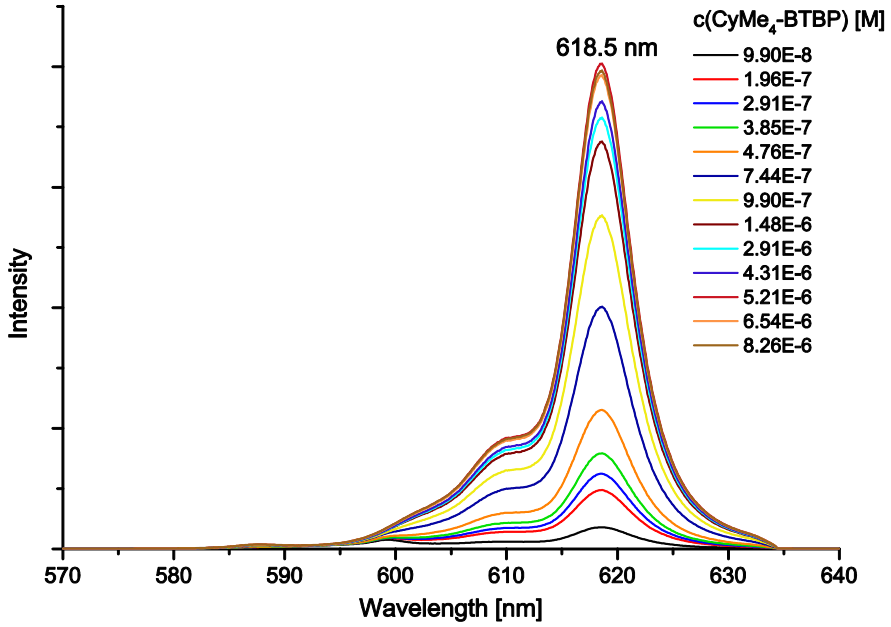

Fig. S7 Fluorescence spectra of Cm(III) in methanol (with 3.3 mol% water) upon increasing $CyMe_4$-BTBP concentration ($c(Cm(III))_{ini} = 5 \cdot 10^{-8}$ M, $c(CyMe_4\text{-BTBP}) = 9.90 \cdot 10^{-8}$ M – $8.26 \cdot 10^{-6}$ M, $c(H^+) = 91.2$ mM).

Speciation diagram

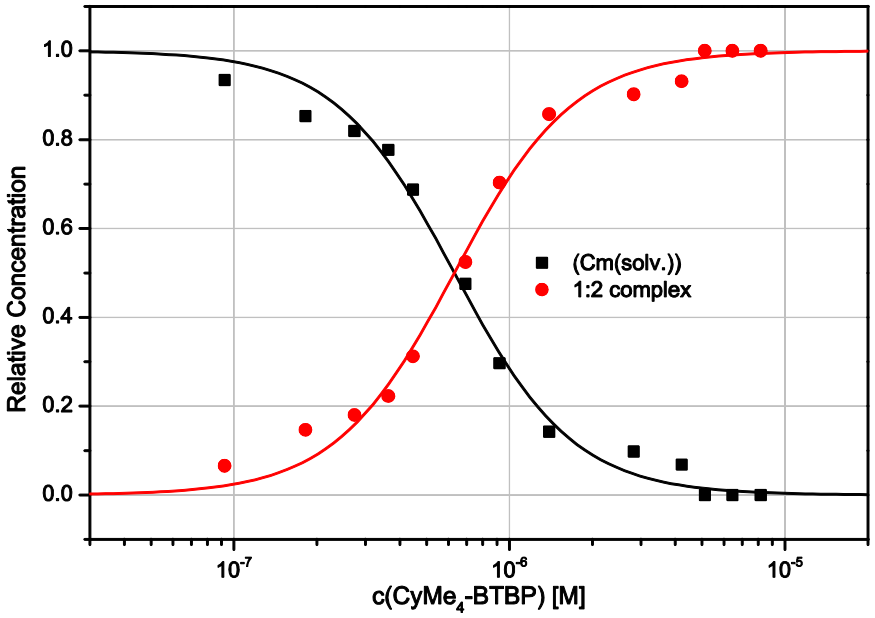

Fig. S8 Relative concentrations of (Cm(solv.)) and the Cm(III)-$CyMe_4$-BTBP 1:2 complex as a function of the free $CyMe_4$-BTBP concentration in methanol (with 3.3 mol% water). Symbols represent experimental data, lines designate calculations.

Overview Eu(III) batch experiments

Table S2 Overview of Eu(III) batch experiments performed with $CyMe_4$-BTPhen and $CyMe_4$-BTBP.

experiment name	emission band(s)	log β_2	average
Eu-BTPhen 1	$^7F_1$ and $^7F_2$	11.9	11.6
	$^7F_0$	12.0	
Eu-BTPhen 2	$^7F_1$ and $^7F_2$	11.2	
	$^7F_0$	11.3	
Eu-BTBP 1	$^7F_1$ and $^7F_2$	11.6	11.3
	$^7F_0$	11.6	
Eu-BTBP 2	$^7F_1$ and $^7F_2$	11.0	
	$^7F_0$	11.0	
Eu-BTBP 3	$^7F_1$ and $^7F_2$	11.3	
	$^7F_0$	11.3	

Batch experiment Eu(III) – $CyMe_4$-BTPhen – slope analysis

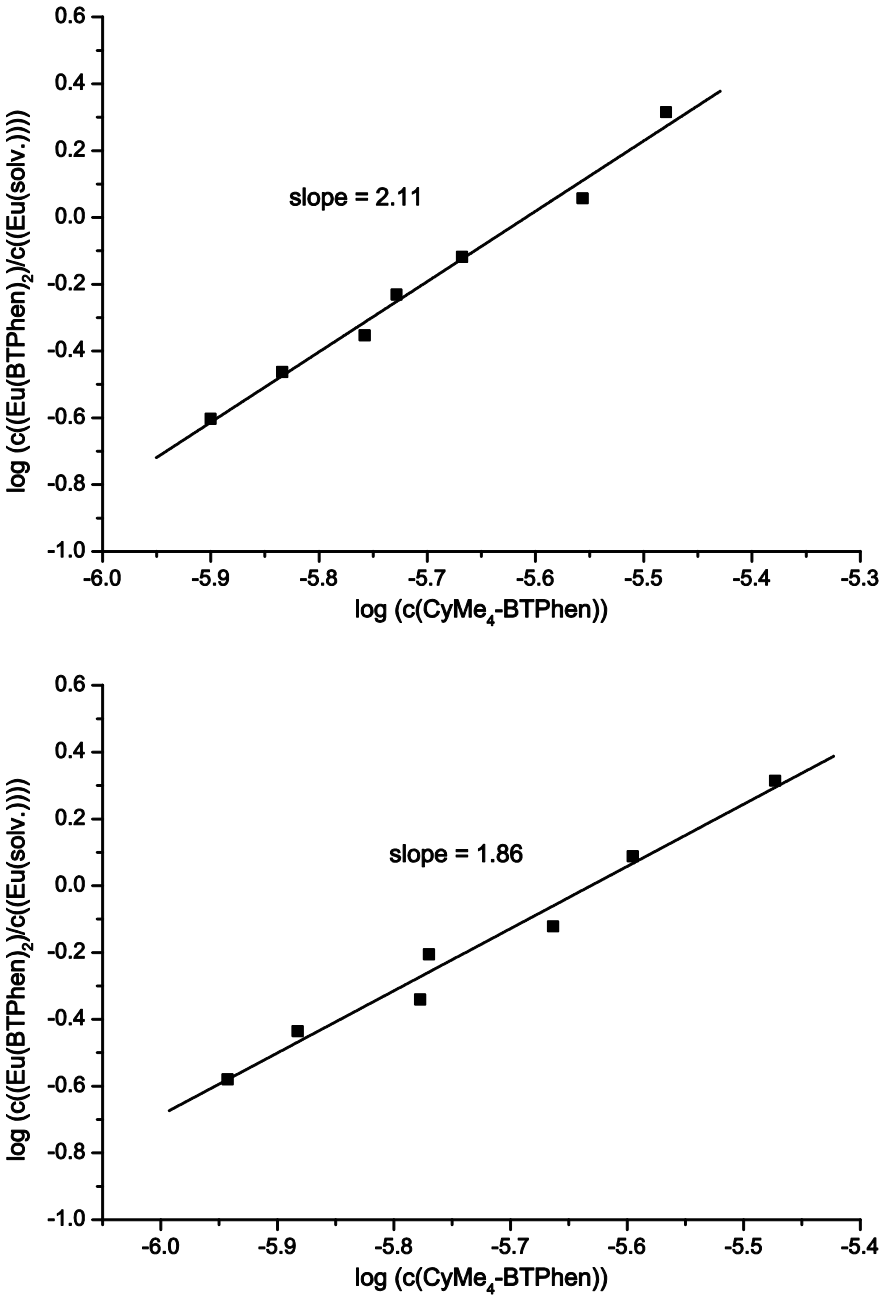

Fig. S9 Double logarithmic plot of c((Eu($CyMe_4$-BTPhen)$_2$))/c((Eu(solv.)) concentration ratio vs free ligand concentration resulting from the analysis of the $^5D_0 \rightarrow {}^7F_1$ and $^5D_0 \rightarrow {}^7F_2$ emission bands (top) or $^5D_0 \rightarrow {}^7F_0$ emission band (bottom).

Batch experiments Eu(III) – $CyMe_4$-BTBP

Emission spectra

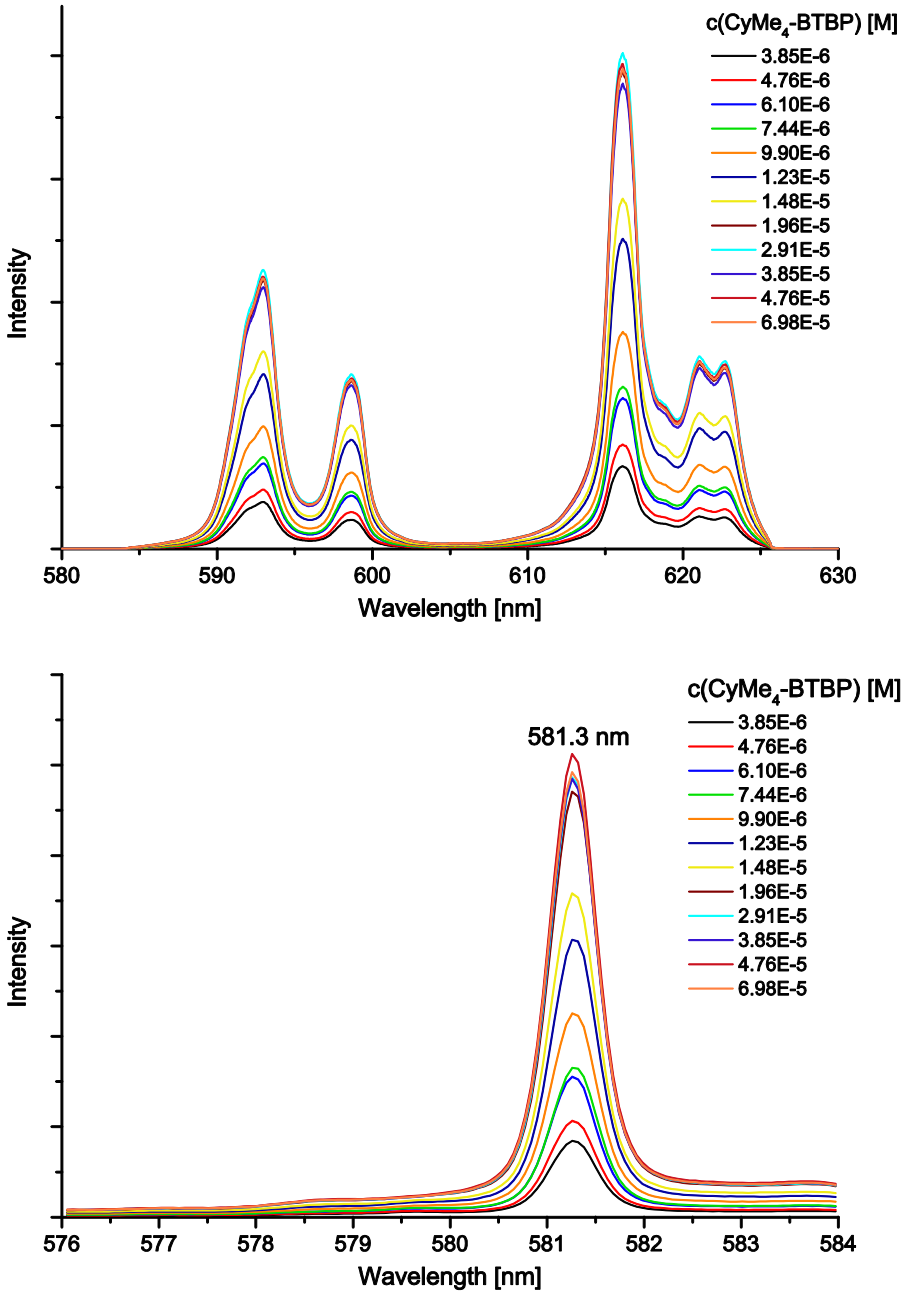

Fig. S10 Fluorescence spectra resulting from the $^5D_0 \rightarrow {}^7F_1$ and $^5D_0 \rightarrow {}^7F_2$ transitions (top) or $^5D_0 \rightarrow {}^7F_0$ transition (bottom) of Eu(III) in methanol (with 3.3 mol% water) upon increasing $CyMe_4$-BTBP concentration ($c(Eu(III))_{ini} = 5 \cdot 10^{-8}$ M, $c(CyMe_4\text{-BTBP}) = 3.85 \cdot 10^{-6}$ M – $6.98 \cdot 10^{-5}$ M, $c(H^+) = 91.2$ mM).

Speciation diagram

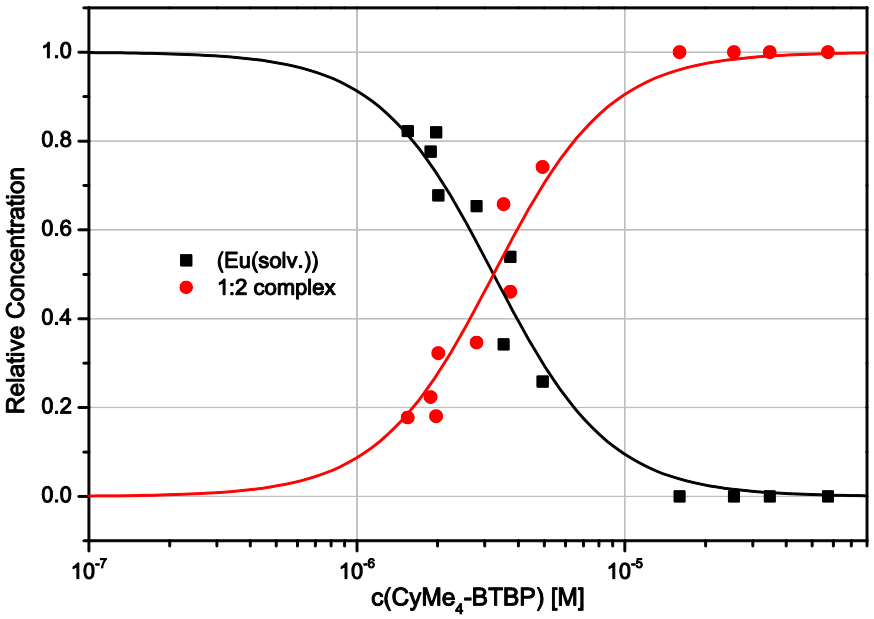

Fig. S11 Relative concentrations of (Eu(solv.)) and the Eu(III)-$CyMe_4$-BTBP 1:2 complex as a function of the free $CyMe_4$-BTBP concentration in methanol (with 3.3 mol% water). Symbols represent experimental data resulting from the analysis of the $^5D_0 \rightarrow {}^7F_1$ and $^5D_0 \rightarrow {}^7F_2$ emission bands, lines designate calculations.

Slope analysis

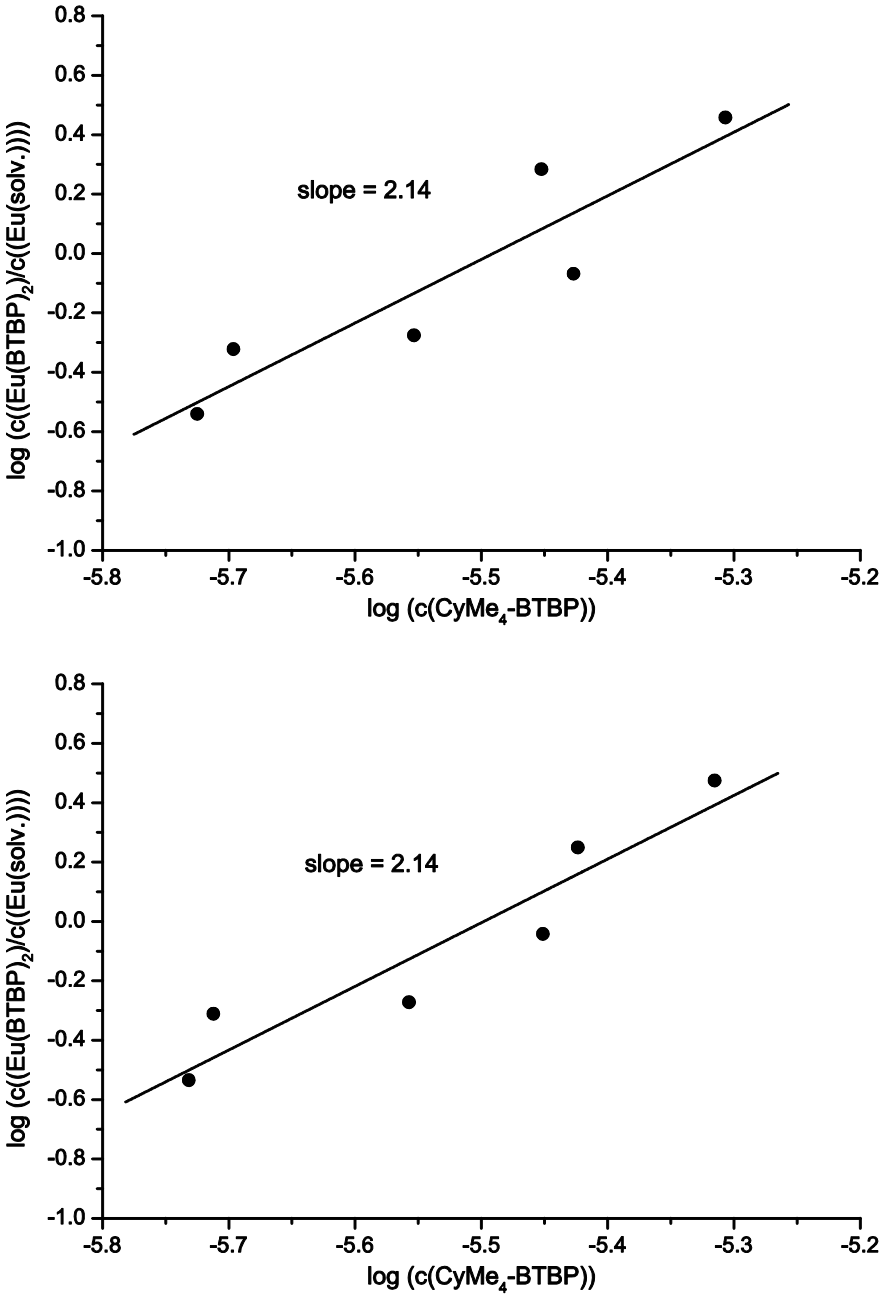

Fig. S12 Double logarithmic plot of c((Eu(CyMe$_4$-BTBP)$_2$))/c((Eu(solv.)) concentration ratio vs free ligand concentration resulting from the analysis of the $^5D_0 \rightarrow {}^7F_1$ and $^5D_0 \rightarrow {}^7F_2$ emission bands (top) or $^5D_0 \rightarrow {}^7F_0$ emission band (bottom).

Comparison of mono- and biphasic experiments with $CyMe_4$-BTBP

Cm(III)

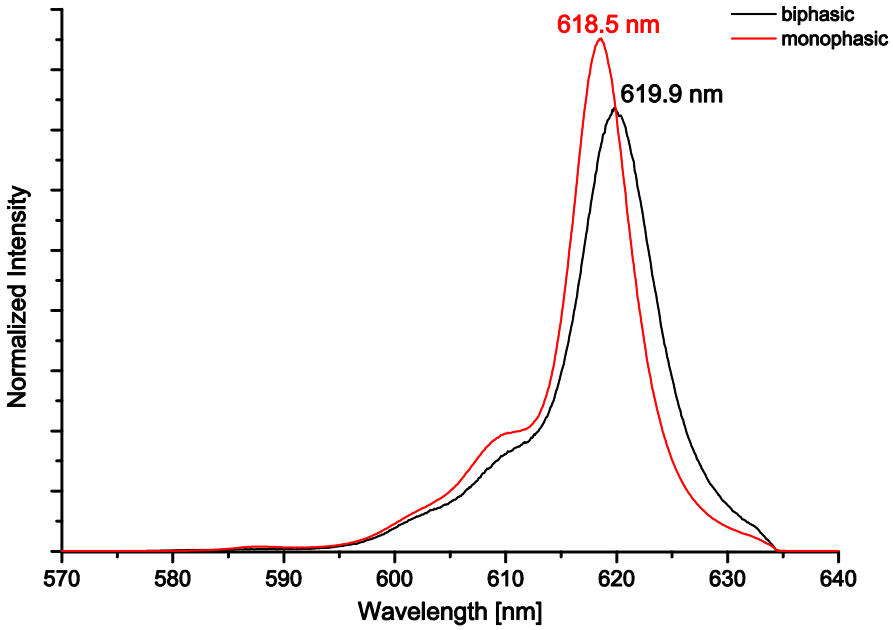

Fig. S13 Normalized fluorescence spectra of Cm(III) in the organic phase of an extraction experiment with $CyMe_4$-BTBP and of the Cm(III)-$CyMe_4$-BTBP 1:2 complex in methanol (with 3.3 mol% water).

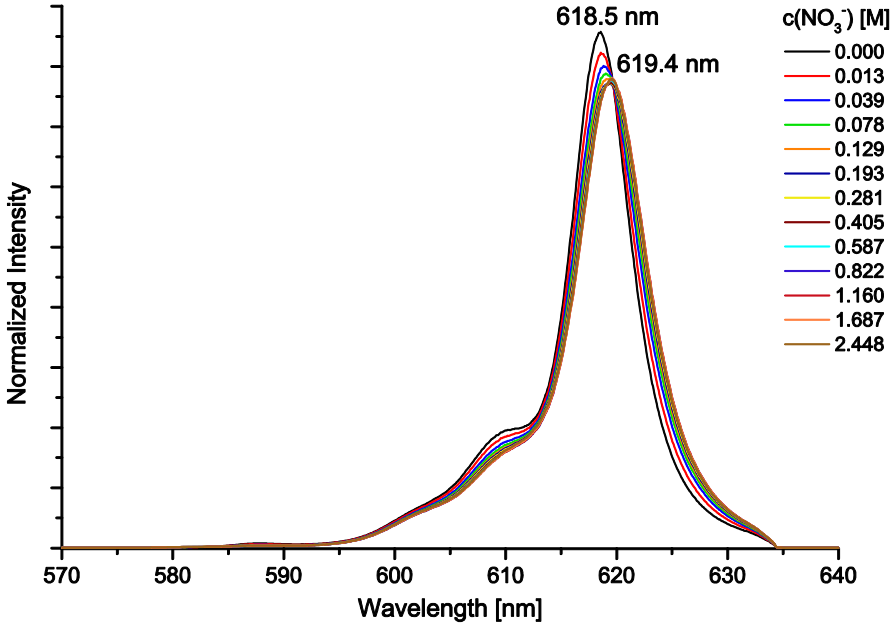

Fig. S14 Normalized fluorescence spectra of Cm(III)-$CyMe_4$-BTBP species upon increasing nitrate concentration in methanol (3.3 mol% water, $c(Cm(III))_{ini} = 4.59 \cdot 10^{-8}$ M, $c(CyMe_4\text{-}BTBP)_{ini} = 8.26 \cdot 10^{-6}$ M).

Eu(III)

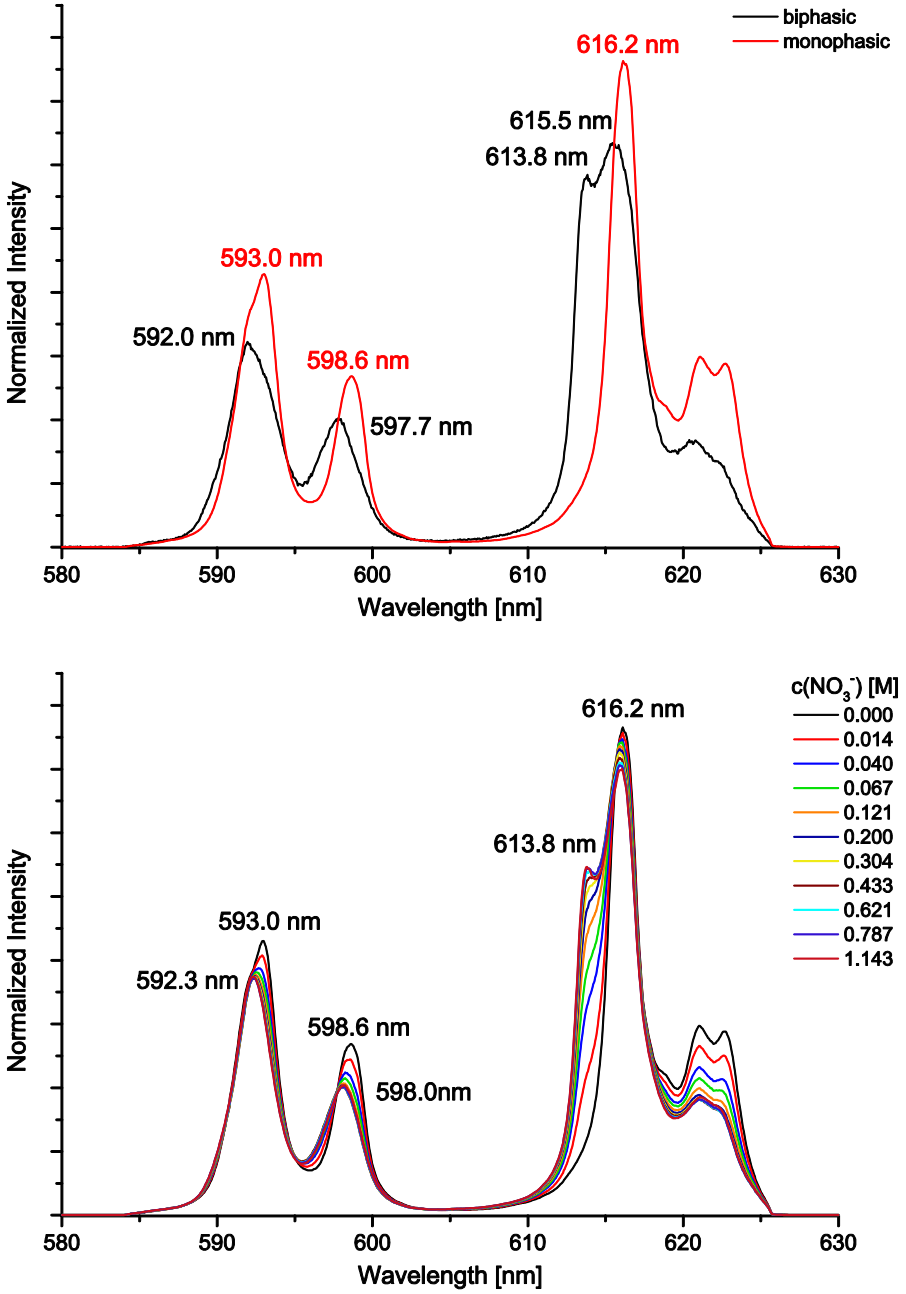

Fig. S15 Normalized fluorescence spectra resulting from the $^5D_0 \rightarrow {}^7F_1$ and $^5D_0 \rightarrow {}^7F_2$ transitions of Eu(III) in the organic phase of an extraction experiment with $CyMe_4$-BTBP and of the Eu(III)-$CyMe_4$-BTBP 1:2 complex in methanol (with 3.3 mol% water) (top). Normalized fluorescence spectra resulting from the $^5D_0 \rightarrow {}^7F_1$ and $^5D_0 \rightarrow {}^7F_2$ transitions of Eu(III)-$CyMe_4$-BTBP species upon increasing nitrate concentration in methanol (with 3.3 mol% water, $c(Eu(III))_{ini} = 6.49 \cdot 10^{-6}$ M, $c(CyMe_4\text{-}BTBP)_{ini} = 4.76 \cdot 10^{-5}$ M) (bottom).

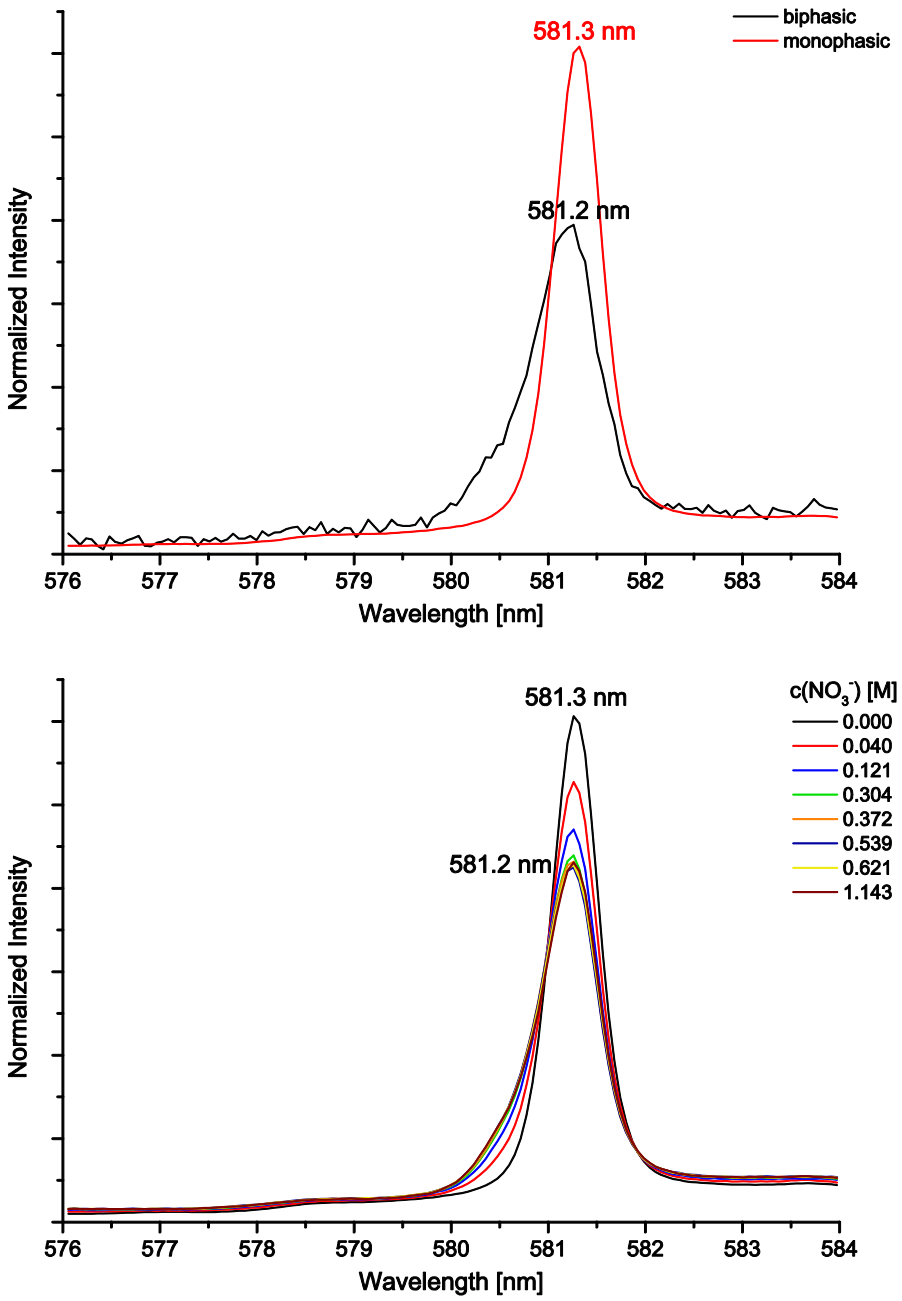

Fig. S16 Normalized fluorescence spectra resulting from the $^5D_0 \rightarrow {}^7F_0$ transition of Eu(III) in the organic phase of an extraction experiment with $CyMe_4$-BTBP and of the Eu(III)-$CyMe_4$-BTBP 1:2 complex in methanol (with 3.3 mol% water) (top). Normalized fluorescence spectra resulting from the $^5D_0 \rightarrow {}^7F_0$ transition of Eu(III)-$CyMe_4$-BTBP species upon increasing nitrate concentration in methanol (with 3.3 mol% water, $c(Eu(III))_{ini} = 6.49 \cdot 10^{-6}$ M, $c(CyMe_4\text{-}BTBP)_{ini} = 4.76 \cdot 10^{-5}$ M) (bottom).