

SUPPORTING INFORMATION

Structural characterization of Am(III) and Pu(III)-DOTA complexes

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UV-visible spectrophotometry

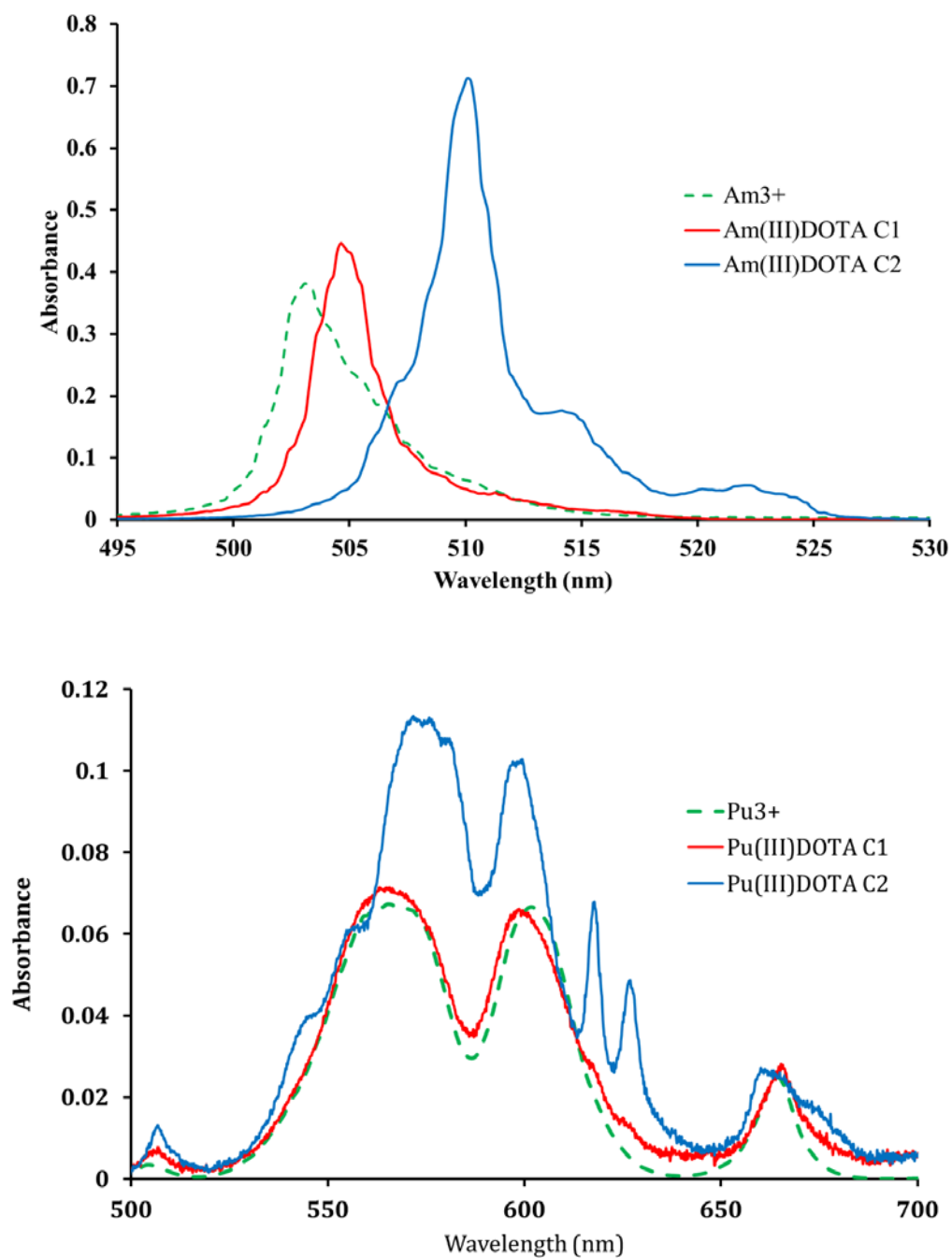


Figure S1 UV-Visible spectra of the C1 and the C2 complexes of the Am(III)-DOTA (top, 10^{-3} M Am^{3+} - 0.1M DOTA) and Pu(III)-DOTA (bottom, $2 \cdot 10^{-3}$ M Pu^{3+} - 0.2M DOTA) complexes in aqueous solution at pH = 3.5 and $\theta = 25^\circ\text{C}$. $l = 1$ cm.

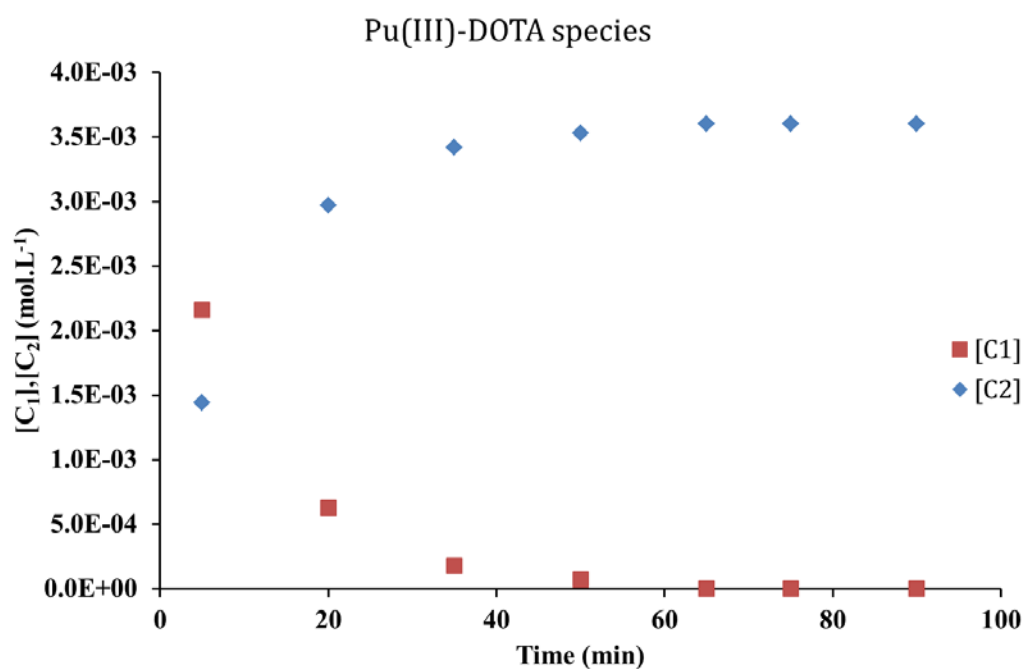
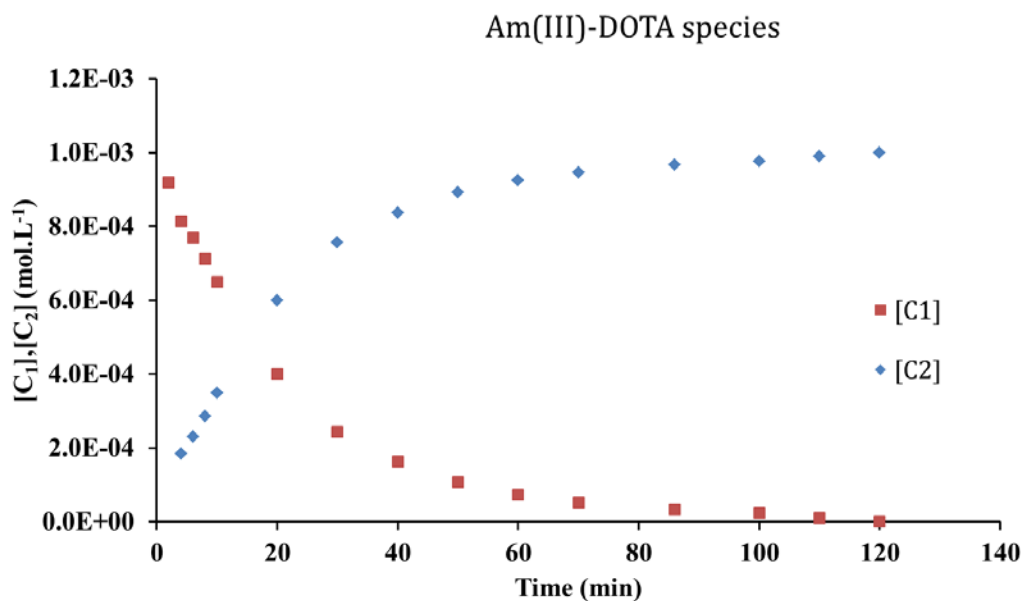


Figure S2. Evolution of complexes C1 and C2 concentration upon complexation of americium(III) by DOTA (top, Composition : Am(III) 10^{-3} M, DOTA 0.2M in aqueous solution : $[\text{NO}_3^-] = 0.07\text{M}$, pH 3.5 ± 0.3 , room temp.) and complexation of plutonium(III) by DOTA (bottom, Composition : Pu(III) $3.6 \cdot 10^{-3}$ M, DOTA 0.2M in aqueous solution : $[\text{Cl}^-] = 0.66$ M, $[\text{ClHA}] = 0.36$ M, pH 3.5 ± 0.3 room temp.).

NMR spectrometry

^1H NMR of DOTA

Proton spectral features of DOTA in water depend highly on the pH. Chemical exchange of the acidic protons at NMR time scale are fast so CH_2 group of the acetate arms and ethylenic ring appear in two peaks at 3.78 and 3.28ppm with an integration ratio of 1:2 respectively ⁶⁶. When the aqueous phase turns more basic, chemical shift of the acetate arms move first to high field but more important change occurs beyond 4 molar NaOH equivalent (Figure S3) since ethylenic protons on the ring become magnetically inequivalent.

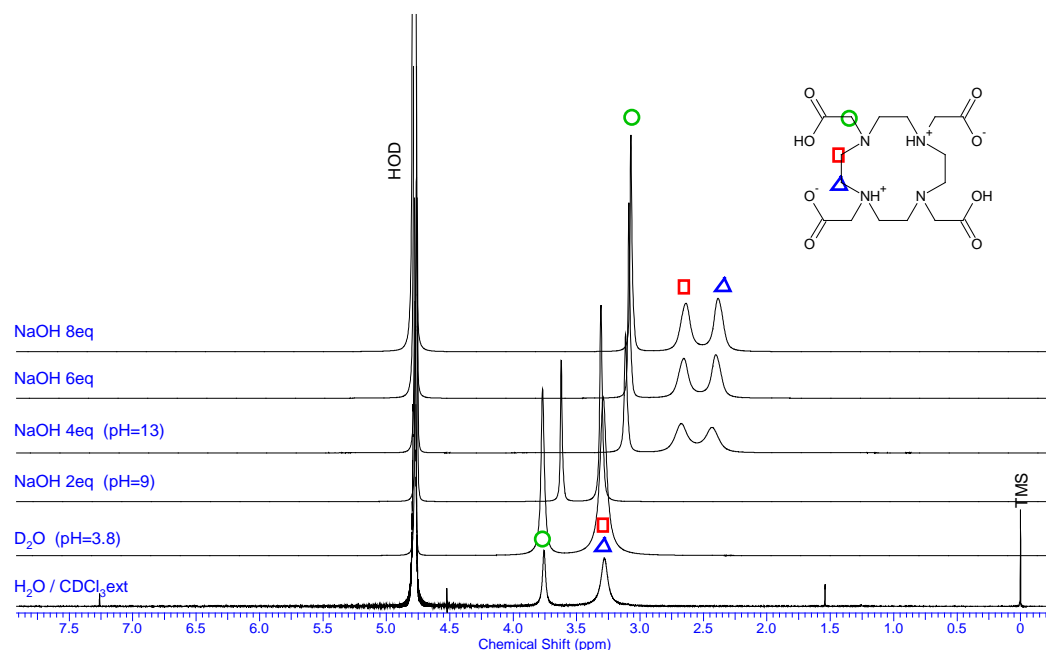


Figure S3 : ^1H NMR spectra of 0.01M DOTA in water with different NaOH concentrations (from 0 to 8 DOTA equivalents). ^1H assignments are depicted with geometric labels. A CDCl_3 external reference with TMS is used for scale calibration (bottom). Spectra recorded at 25°C .

^1H NMR of Pu^{III} -DOTA

^1H NMR spectra recorded on a 25mM DOTA in D_2O solution in presence of Pu(III) nitrate (with a ratio $[\text{DOTA}]/[\text{Pu(III)}]=5$) at pH 2 exhibit only two signals at 3.72 and 3.18 ppm in a ratio 1:2. They are then assigned to the acetate arms and ethylenic protons of the DOTA ring respectively. Spectral features change after addition of ammonia aliquots (Figure S4): At pH 6 a few broad peaks appear as well as a chemical shift change of the acetate protons. Broad peaks are assigned to the C2 Pu(III)-DOTA complex while the slight shift (from 0.06 to 0.1ppm toward low fields) and intensity increase (1.2:2) of the acetate signal is assigned to a mixture of free DOTA and C1 Pu(III)-DOTA complex. C1 complex arises from possible binding effect of the acetate arm with the Pu(III) cation. After several hours no other significant NMR spectral change is observed presumably because part of the plutonium precipitated after the addition of ammonia. This explanation is supported by the disappearance of the Pu^{III} wavelength at 561nm. In order to avoid plutonium hydrolysis as much as possible another sample is prepared at pH 4. Recorded ^1H NMR spectra exhibit clearly 5 broad peaks assigned to the C2 Pu(III)-DOTA complex but also 4 new finely resolved peaks (Figure S5). Integration ratio of both peak series evolve in time: Integration of the sharp peaks grow from 28% to 35% in 2 days while the broad ones decrease accordingly. UV-visible spectrometry performed simultaneously suggests the presence of Pu^{IV} species owing to the appearance of a new wavelength at 507nm. Furthermore this absorbance increases in time and exhibits a good correlation with integration ratios measured from ^1H NMR. Consequently the sharp NMR signals observed can be assigned to the Pu^{IV} -DOTA complex. More accurate NMR assignments will be done in a further work.

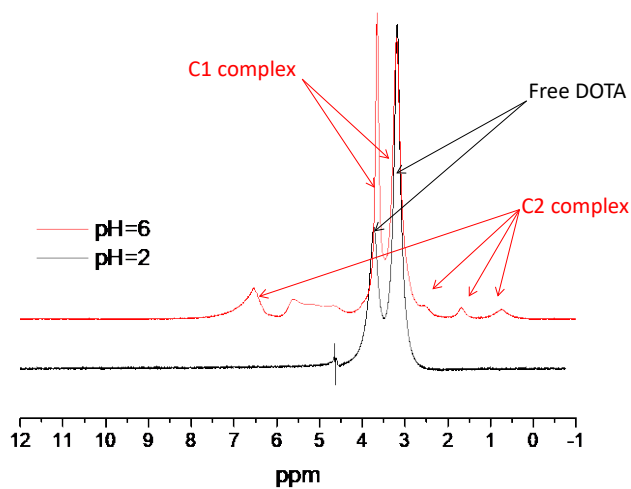


Figure S4: ^1H NMR spectra of 25mM DOTA in D_2O with Pu(III) at different pH values. $[\text{DOTA}]/[\text{Pu}^{\text{III}}]=5$. Water suppression with WET1D pulse sequence.

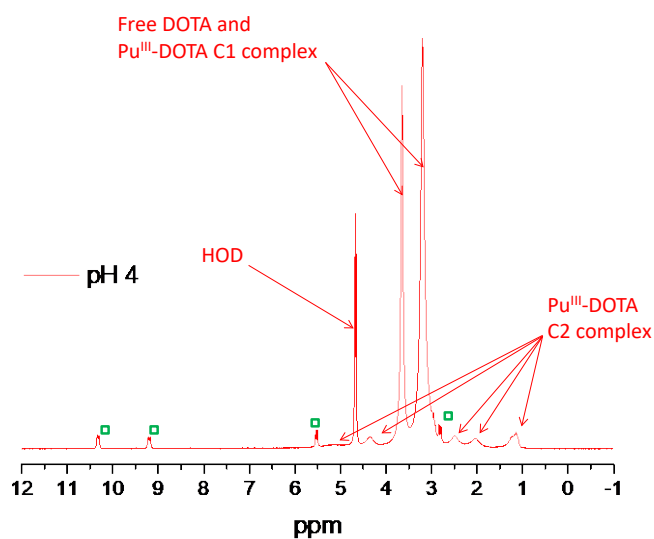


Figure S5: ^1H NMR spectra of 25mM DOTA in D_2O with Pu(III) at pH 4. $[\text{DOTA}]/[\text{Pu}^{\text{III}}]=5$. Red arrows point Pu^{III}-DOTA complexes and free DOTA. Green squares indicate signals of

Pu^{IV}-DOTA complex. WET1D pulse sequence is used for water suppression but incompletely achieved.

DFT Calculations

Table S1: Selected bond distances in $M(\text{DOTA})(\text{H}_2\text{O})^-$ (C2, $M = \text{Nd}^{3+}, \text{Am}^{3+}$) for TSAP and SAP isomers (average distances in Å) and free energy differences for the isomer equilibrium reaction $\text{TSAP} \leftrightarrow \text{SAP}$ (ΔG^0 in kJ mol^{-1} , $T=298 \text{ K}$). DFT/B3LYP calculations in aqueous solution.

M	TSAP			SAP			DG^0
	M-O _{DOTA}	M-N _{DOTA}	M-O _{water}	M-O _{DOTA}	M-N _{DOTA}	M-O _{water}	
Nd	2.419	2.773	2.712	2.408	2.761	2.665	+9
Am	2.435	2.733	2.772	2.404	2.773	2.681	+13

Table S2: QTAIM data in $M(\text{DOTA})(\text{H}_2\text{O})^-$ (TSAP), values of density ρ , Laplacian $\nabla^2\rho$, and total energy density H at the BCPs in a.u. DFT/B3LYP calculations in the gas phase and in aqueous solution.

Bond	gas			sol		
	ρ	$\nabla^2\rho$	H	ρ	$\nabla^2\rho$	H
Nd-O _{DOTA}	0.0572	0.2178	-0.00199	0.0539	0.2042	-0.00124
Am-O _{DOTA}	0.0593	0.2424	-0.00227	0.0542	0.2178	-0.00164
Pu-O _{DOTA}	0.0605	0.2468	-0.00193	0.0548	0.2175	-0.00142
Nd-N _{DOTA}	0.0236	0.0712	0.00085	0.0305	0.0885	0.00012
Am-N _{DOTA}	0.0249	0.0746	-0.00014	0.0351	0.1037	-0.00123
Pu-N _{DOTA}	0.0237	0.0694	-0.00029	0.0340	0.1023	-0.00103
Nd-O _{wat}	0.0355	0.1217	0.00030	0.0285	0.0953	0.00050
Am-O _{wat}	0.0383	0.1376	-0.00054	0.0265	0.0891	-0.00033
Pu-O _{wat}	0.0373	0.1291	-0.00055	0.0271	0.0909	-0.00045

Table S3: QTAIM data in $M(\text{H}_2\text{O})_9^{3+}$, values of density ρ , Laplacian $\nabla^2\rho$, and total energy density H at the BCPs in a.u. DFT/B3LYP calculations in the gas phase and in aqueous solution.

Bond	gas			sol		
	ρ	$\nabla^2\rho$	H_b	ρ	$\nabla^2\rho$	H
Nd-O _{wat}	0.0364	0.1417	0.00196	0.0401	0.1601	0.00197
Am-O _{wat}	0.0382	0.1557	0.00125	0.0419	0.1768	0.00130
Pu-O _{wat}	0.0377	0.1531	0.00134	0.0414	0.1739	0.00146