Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Effect of Metal Complexation on TODGA Radiolysis: A Comparison between Ex-Situ Gamma and In-Situ Alpha Irradiation

Ashleigh Kimberlin[a], Georges Saint-Louis[a], Dominique Guillaumont[a], Béatrice Camès[a], Philippe Guilbaud[a], and Laurence Berthon*[a]

Supplemental Informations

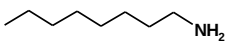
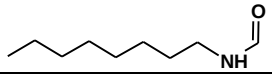
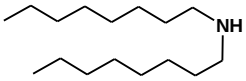
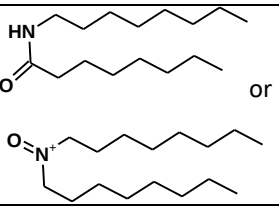
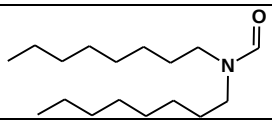
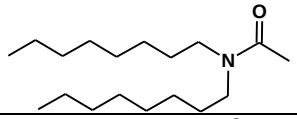
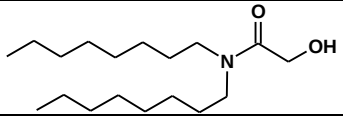
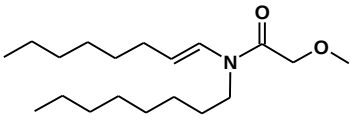
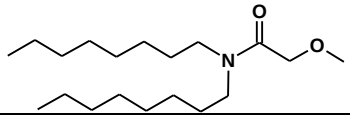
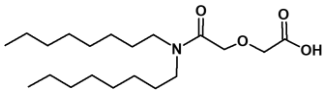
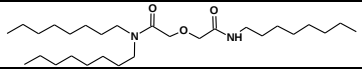
Table S1: Extracted Nd concentrations in the UV-Vis solutions determined by ICP-AES.

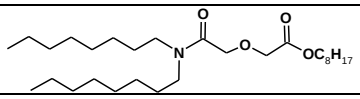
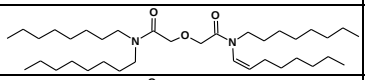
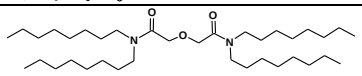
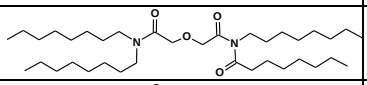
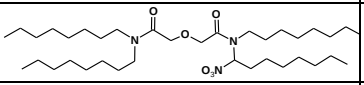
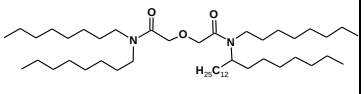
	Organic phase	Aqueous phase	Dose (kGy)	C_{Nd} (mmol L^{-1})	C_{Nd} * (mmol L^{-1})
3	0.1 mol L^{-1} TODGA in dodecane + 5%$_{Vol}$ octanol	1 mmol L^{-1} Nd in 2.5 mol L^{-1} HNO_3	265	0.50	7.5
4			505	0.78	9.3
5		10 mmol L^{-1} Nd in 2.5 mol L^{-1} HNO_3	227	9.9	
6			451	9.3	
7		30 mmol L^{-1} Nd in 2.5 mol L^{-1} HNO_3	221	29.3	
8			448	28.3	

*Solutions were made by contacting solutions 3 and 4 post-irradiation with an equal volume of approx. 17 mmol L^{-1} Nd in 2.5 mol L^{-1} HNO_3.

Table S2: Complete list of peaks found in ESI-MS spectra. Some peaks remain unassigned. The numbers refer to the solution conditions detailed in Table 1. The conditions are also listed under the name where octOH = 5 %$_{Vol}$ 1-octanol, x mol L^{-1} HNO_3 = concentration of HNO_3 in the precontact.

Number 0-8 refer to Nd solutions. Nd/Am refers to if the product has appeared in an ion peak with Nd(III) or Am(III). References are literature sources in which the degradation product has previously been identified as a radiolysis product of DGA.

DP	Proposed Structure	LH^+ m/z	LNa^+ m/z	**0**	1-2 Dod 1mM Nd 1M HNO_3	3-4 1mM Nd OctOH 2.5M HNO_3	5-8 10-30 mM Nd octOH 2.5M HNO_3	Am 1mM	Am 10mM	Comments	Ref.
I		130	152	*	*	*	*	*	*	High instrument response factor	[1]
II		157	179	*	*	*					[1]
		200		*		*					
		210		*	ε	ε					
		240		*	ε						
III		242	264	*	*	*	*	*	*	High instrument response factor	[1-8]
		255		*	*	*					
IV		256	278	*			*		*	Oxygen location debatable	[1,3]
		267	289	*	*	*					
V		270	292	*	ε	ε	*		*		[1-9]
VI		284	306	*	*	*	*	*	*		[1-9]
VII		300	322	*	*	*	*		*		[1-9]
		312	334	*	ε	ε	*	*		location of double bond unknown or pollution ?	
VIII		314	336	*			*			30mM Nd Results from radiolytic split,	[1,2,9]
		338		*	ε	ε					
		340			*						
		348							*	*dicharged*	
IX		358	380	*			*				[1,2,4,6-9]
X		469	491	*	*	*	*	*	*	*LK^+ : 507*	[1,4-7,9]

XI		470	492	*			*	*	*	*LK⁺ : 508*	[1,4]
XIV									*		
	 **TODGA**	**581**	**603**	*	*	*	*	*	*	***LK⁺ : 619***	
XII		595	617	*			ε			*LK⁺ : 633*	[1]
XV		642	664							Only seen in Nd/Am complexes	
XIII		751	773							Only seen in Nd complexes, dodecyl location variable	[1]

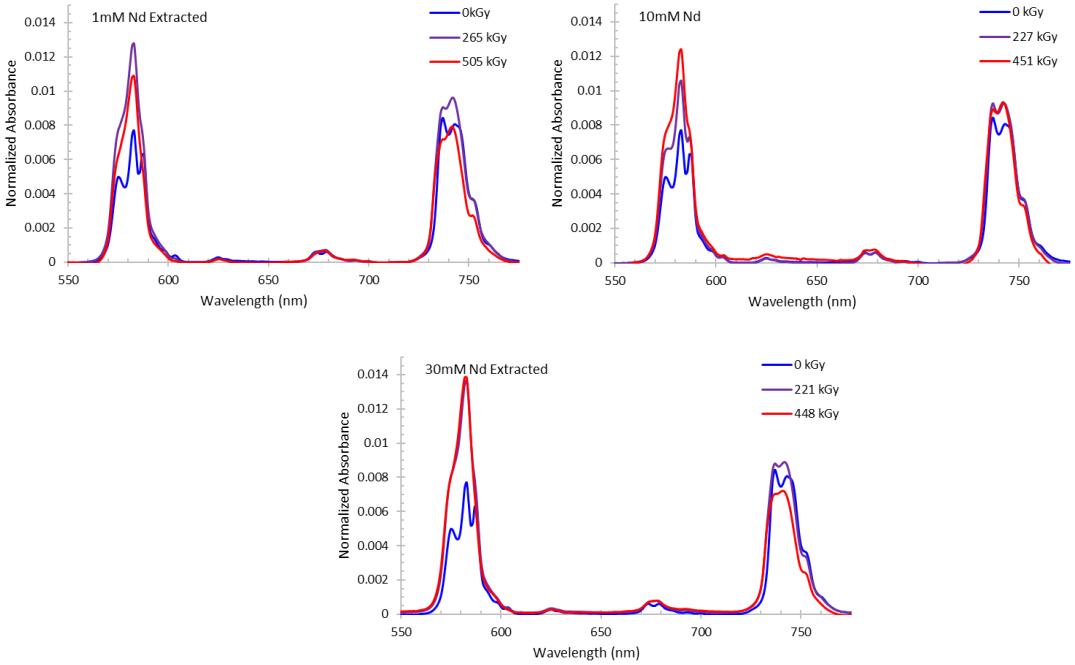


Figure S1: UV-Vis spectra of gamma irradiated TODGA solutions containing Nd. All spectra were background corrected and concentration normalized (using concentration obtained from ICP-AES). The solution containing 1 mmol L^{-1} Nd was irradiated with 1 mmol L^{-1}, but an additional 5-7mmol.L^{-1} Nd was added via contact with 17 mmol L^{-1} Nd in 2.5 mol L^{-1}M HNO_3 to improve the quality of the spectrum (The composition of the irradiated solutions is reported in Table S1).

<u>Comments:</u>

The 585 nm peak in the 1mM Nd solution increased at 250 kGy, but less than the other two solutions or the blank solution. The peak stayed this height at 500 kGy, but the shoulder peaks decreased. The 740nm peak followed the blank fairly closely, first increasing in intensity and then decreasing to below the T_0 spectrum, while inverting the ratio of 736nm and 744nm. This peak moved more than the blank spectrum, which stopped roughly the same intensity as the T_0 spectrum.

In the 10mM Nd solution, the 585 nm peak increased like in the other solutions, but with less the relative decrease in the 587nm and 575 nm peaks. Additionally, the peak at 740nm increased, but has yet to decrease again at 500kGy. This all seems to suggest that the 10mM Nd solution is less degraded than the 1mM Nd solution.

The 30mM solutions appears to have different products than the other solutions. The 585nm peak rose to its final height after only 250kGy, but the peak at 745 nm did not rise as much as the other peaks. Alternatively, it could be that the 745nm peak increased to its max height at a lower dose and is beginning its path downwards at 250kGy. The 500kGy spectrum shows that the ratio of 736nm and 744nm did not invert as in other spectra, even though the intensity of the transition is less than the other solutions. Most likely this is due to another product complexing the Nd that is not present in the other solutions, perhaps DPIX (the addition of NO_3 onto TODGA).

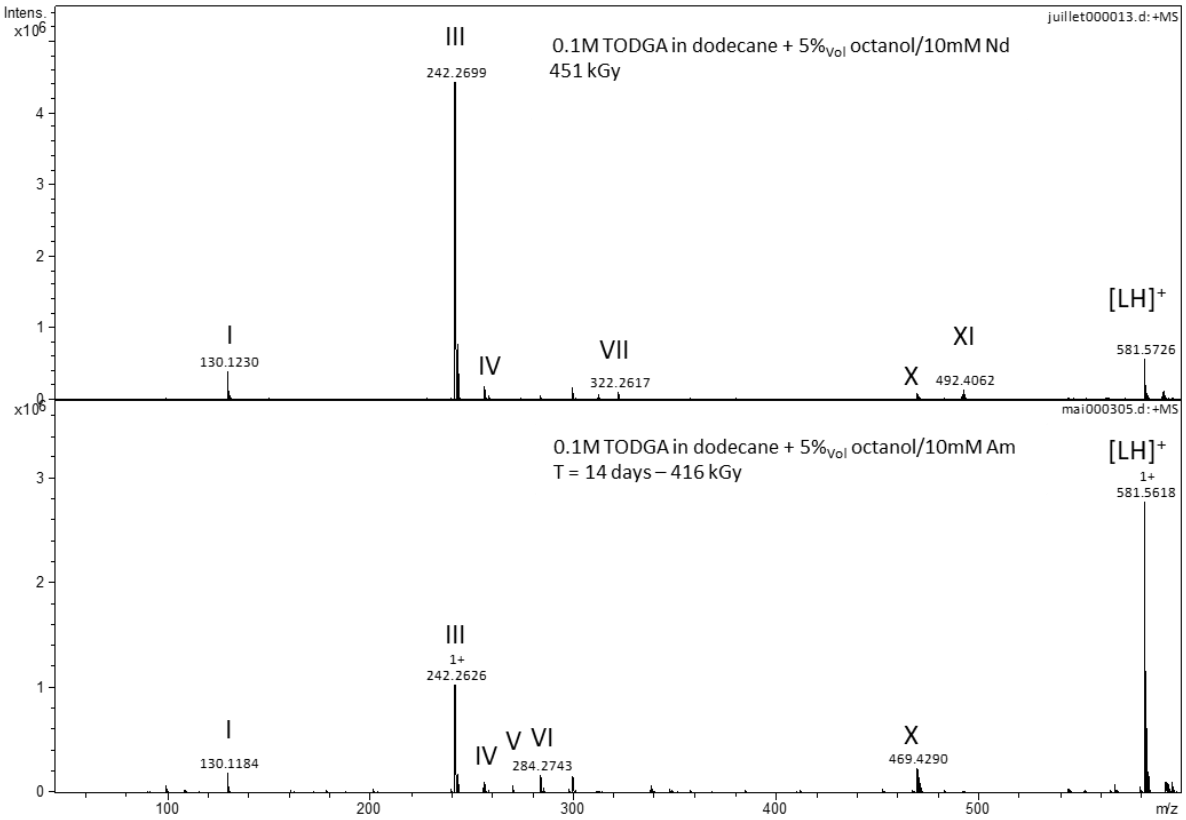


Figure S2: ESI-MS spectra (low mass range) of TODGA solutions (top) loaded with 10 mmol L^{-1} of Nd (gamma ex-situ irradiation at ≈ 450 kGy) or (bottom) 10 mmol L^{-1} of Am (alpha in-situ irradiation at ≈ 420 kGy). Conditions: Org phase: 0.1 mol L^{-1} TODGA in dodecane + 5% octanol Aq Phase: Nd(III) or Am(III) in 2.5 mol L^{-1} HNO_3.

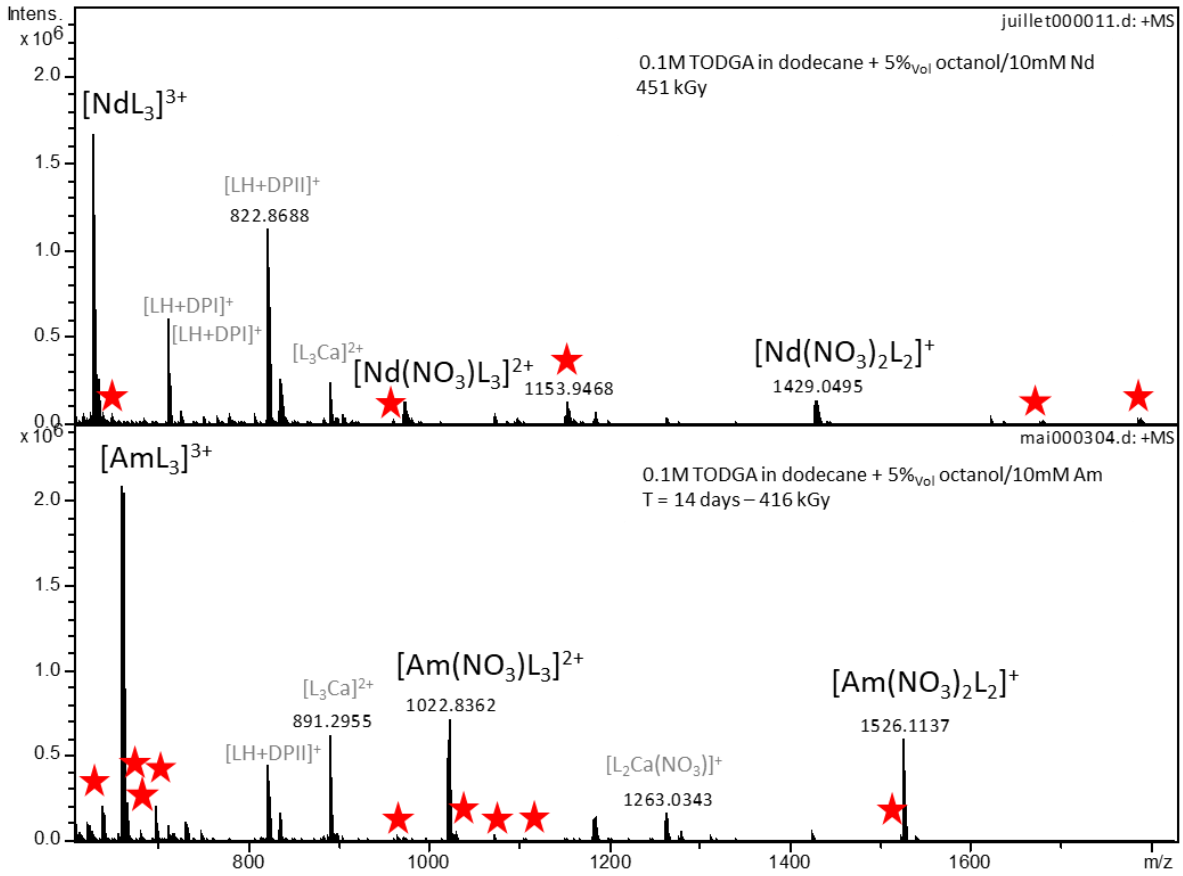


Figure S3: ESI-MS spectra (high mass range) of TODGA solutions (top) loaded with 10 mmol L^{-1} of Nd (after gamma ex-situ irradiation at ≈ 450 kGy) or (bottom) 10 mmol L^{-1} of Am (alpha in-situ irradiation at ≈ 420 kGy).

Conditions: Org phase: 0.1 mol L^{-1} TODGA in dodecane + 5% octanol Aq Phase: Nd(III) or Am(III) in 2.5 mol L^{-1} HNO_3.

Ion at 822 m/z is assigned to an adduct formed between TODGA and DP III. Non labeled peaks are H^+, Na^+, and Ca^{2+} adducts of TODGA and its degradation products.

[1] Kimberlin, A.; Guillaumont, D.; Arpigny, S.; Camès, B.; Guilbaud, P.; Saint-Louis, G.; Galán, H.; Berthon, L. *New Journal of Chemistry* **2021**, *45*, 12479.

[2] Sugo, Y.; Sasaki, Y.; Tachimori, S. *Radiochimica Acta* **2002**, *90*, 161.

[3] Galan, H.; Zarzana, C. A.; Wilden, A.; Nunez, A.; Schmidt, H.; Egberink, R. J. M.; Leoncini, A.; Cobos, J.; Verboom, W.; Modolo, G.; Groenewold, G. S.; Mincher, B. J. *Dalton Transactions* **2015**, *44*, 18049.

[4] Galan, H.; Nunez, A.; Espartero, A. G.; Sedano, R.; Durana, A.; de Mendoza, J. *Procedia Chemistry* **2012**, *7*, 195.

[5] Hubscher-Bruder, V.; Mogilireddy, V.; Michel, S.; Leoncini, A.; Huskens, J.; Verboom, W.; Galan, H.; Nunez, A.; Cobos, J.; Modolo, G.; Wilden, A.; Schmidt, H.; Charbonnel, M. C.; Guilbaud, P.; Boubals, N. *New Journal of Chemistry* **2017**, *41*, 13700.

[6] Roscioli-Johnson, K. M.; Zarzana, C. A.; Groenewold, G. S.; Mincher, B. J.; Wilden, A.; Schmidt, H.; Modolo, G.; Santiago-Schübel, B. *Solvent Extraction and Ion Exchange* **2016**, *34*, 439.

[7] Sánchez-García, I.; Galán, H.; Perlado, J. M.; Cobos, J. *EPJ Nuclear Sci. Technol.* **2019**, *5*, 19.

[8] Sharma, J. N.; Ruhela, R.; Singh, K. K.; Kumar, M.; Janardhanan, C.; Achutan, P. V.; Manohar, S.; Wattal, P. K.; Suri, A. K. *Radiochimica Acta* **2010**, *98*, 485.

[9] Zarzana, C. A.; Groenewold, G. S.; Mincher, B. J.; Mezyk, S. P.; Wilden, A.; Schmidt, H.; Modolo, G.; Wishart, J. F.; Cook, A. R. *Solvent Extraction and Ion Exchange* **2015**, *33*, 431.