Electronic Supplementary Information

2,9-Dicarbonyl-1,10-phenanthroline derivatives with unprecedented Am(III)/Eu(III) selectivity under highly acidic conditions

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Table S1: Distribution coefficients of Am(III) and Eu(III) and separation factors Am/Eu as a function of initial nitric acid. Aqueous phase: [HNO_3] = 0.001 to 3.82 M; Organic phase: [L] = 0.01 or 0.02 M + [Br-cosan] = 0.02 or 0.01 M in NPHE; (mixing time: 60 min, temperature: 22 ± 2°C).

Ligand	AQUEOUS PHASE	ORGANIC PHASE						
	[HNO_3]	1-Octanol	Kerosene	NPHE	[L] / [Br-Cosan] = 0.5 in NPHE	[L] / [Br-Cosan] = 1 in NPHE	[L] / [Br-Cosan] = 2 in NPHE	
1	**0.01**	n.a.	0.017	n.a.	> 1000		515.4	***D-Am***
	0.1	n.a.	n.a.	n.a.	1.45		8.16	
	1	0.0005	n.a.	0.0073	0.0546		0.291	
	3.82	0.0031	0.0265	0.0562	0.0188		0.164	
	0.01	n.a.	0.0157	n.a.	> 1000		62.95	***D-Eu***
	0.1	n.a.	n.a.	n.a.	0.253		0.234	
	1	0.0001	n.a.	0.001	0.0138		0.007	
	3.82	0.0018	0.0087	0.0066	0.0022		0.013	
	0.01	n.a.	1.08	n.a.	n.a.		8.19	***SF Am/Eu***
	0.1	n.a.	n.a.	n.a.	5.74		34.8	
	1	3.5	n.a.	7.62	3.96		41.7	
	3.82	1.68	3.04	8.56	8.71		12.5	
2	**0.001**	n.a.			9.66	2.15	0.0430	***D-Am***
	0.01	n.a.			11.9		0.827	
	0.1	n.a.			1.14		0.0462	
	1	0.0821			0.0085		0.0013	
	3.82	0.0158			n.a.		0.0027	
	0.001	n.a.			0.55	0.124	0.0086	***D-Eu***
	0.01	n.a.			0.962		0.0815	
	0.1	n.a.			0.0759		0.0036	
	1	0.0769			0.0023		0.0002	
	3.82	0.0033			n.a.		0.0004	
	0.001	n.a.			17.7	17.3	5.00	***SF Am/Eu***
	0.01	n.a.			12.3		10.2	
	0.1	n.a.			15.0		12.8	
	1	1.07			3.69		8.86	
	3.82	4.76			n.a.		6.31	
3	**0.01**				0.0634			***D-Am***
	0.1				0.0089			
	3.82				0.0131			
	0.01				0.01			***D-Eu***
	0.1				0.0016			
	3.82				0.0117			
	0.01				6.31			***SF Am/Eu***
	0.1				5.89			
	3.82				1.12			
4	**0.001**	n.a.	n.a.	n.a.	n.a		0.0022	***D-Am***
	0.01	n.a.	0.1236	0.001	1.53		0.0036	
	0.1	n.a.	n.a.	n.a.	0.0568		n.a.	
	1	n.a.	n.a.	n.a.	0.0035		n.a.	
	3.82	0.0019	n.a.	n.a.	0.0055		0.0687	
	0.001	n.a.	n.a.	n.a.	n.a.		0.0018	***D-Eu***
	0.01	n.a.	0.122	0.0007	0.623		0.0046	
	0.1	n.a.	n.a.	n.a.	0.0221		n.a.	
	1	n.a.	n.a.	n.a.	0.0015		n.a.	
	3.82	0.0019	n.a.	n.a.	0.0011		0.0051	
	0.001	n.a.	n.a.	n.a.	n.a.		1.22	***SF Am/Eu***
	0.01	n.a.	1.01	1.43	2.45		0.79	
	0.1	n.a.	n.a.	n.a.	2.57		n.a.	
	1	n.a.	n.a.	n.a.	2.31		n.a.	
	3.82	1	n.a.	n.a.	4.87		13.4	

Note: blank cells = non tested; n.a. = data not available

Figure SI1: ESI-MS of ligand **4** before the contact with HNO_3 3.82 M

- L.G.S. - Laboratorio Grandi Strumenti - Display Report

Analysis Info

Analysis Name	tam idr c1.d	Acquisition Date	04/07/10 15:07:49	Operator	Walter Panzeri
Sample Name		Method	Copy of _awalt1.MS	Instrument	esquire3000plus
Comment	1 mg/ml dil 1:100 MeOH Richiedente: Galletta				

Acquisition Parameter

Ion Source Type	ESI	Mass Range Mode	Std/Normal	Ion Polarity	Positive	Alternating Ion Polarity	off
Scan Begin	50 m/z	Scan End	1000 m/z	Averages	5 Spectra	Accumulation Time	30 µs
Capillary Exit	151.0 Volt	Skim 1	40.0 Volt	Trap Drive	67.7	Auto MS/MS	off

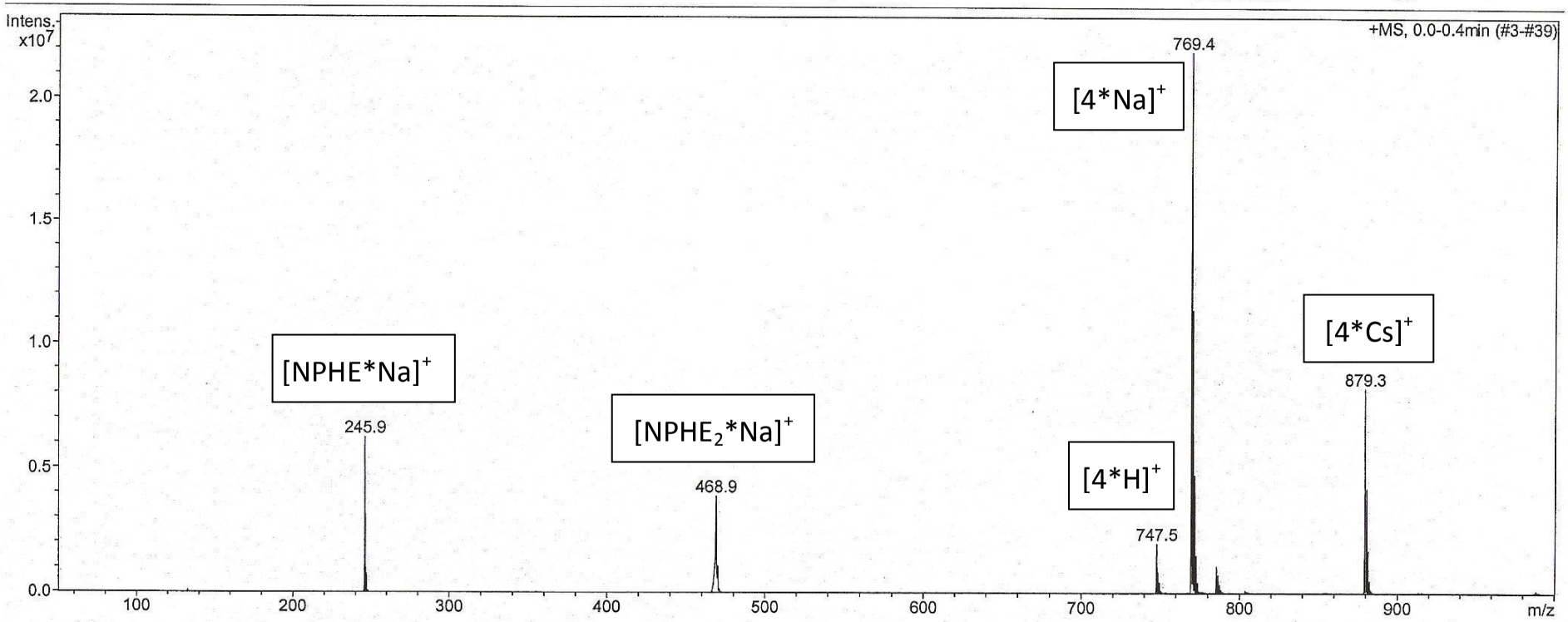

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Figure SI2: ESI-MS of ligand **4** after the contact with HNO_3 3.82 M

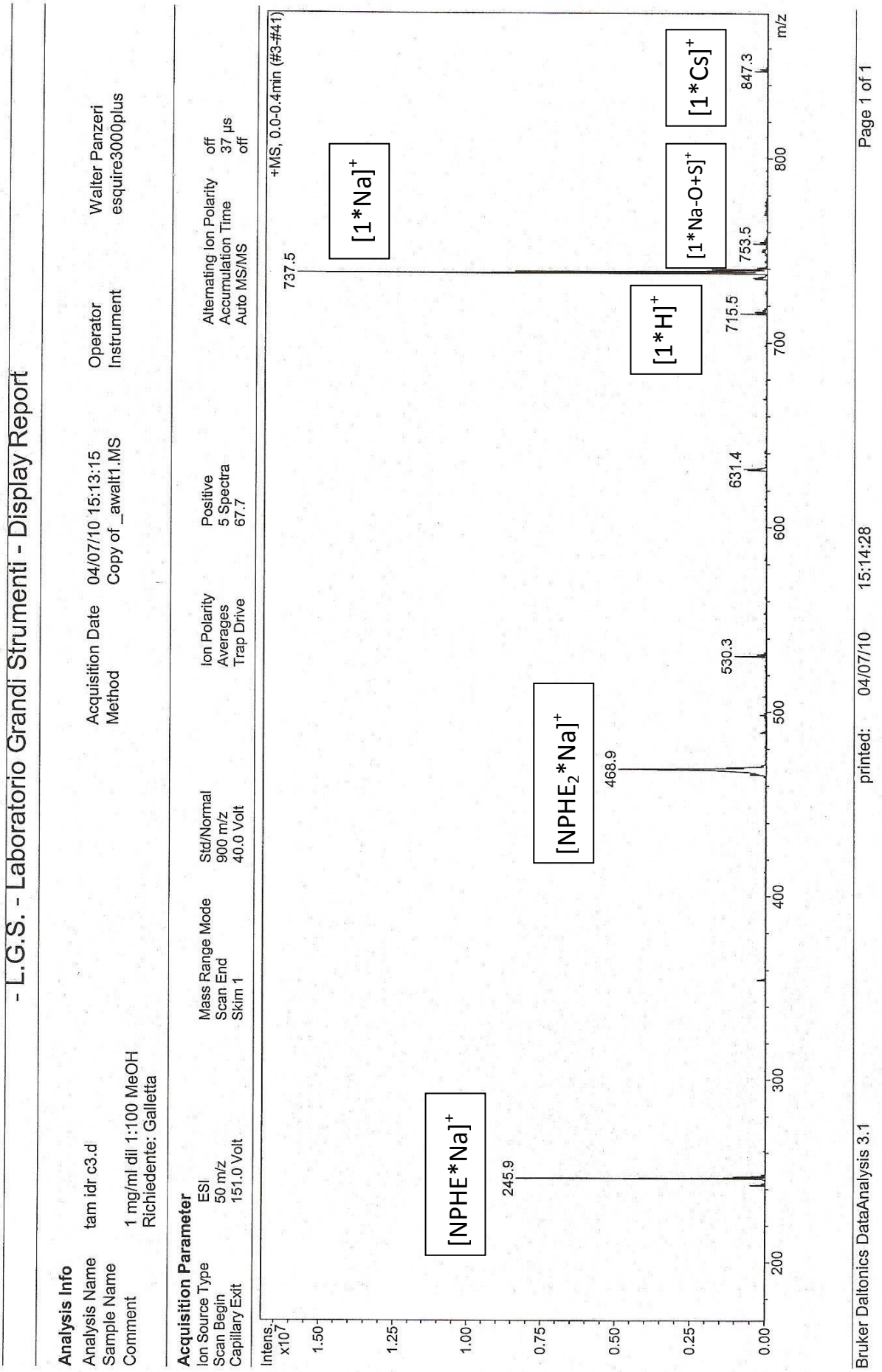

Figure SI3: ESI-MS of a solution containing ligand **4** and Eu nitrate in methanol in the ratio 1:10

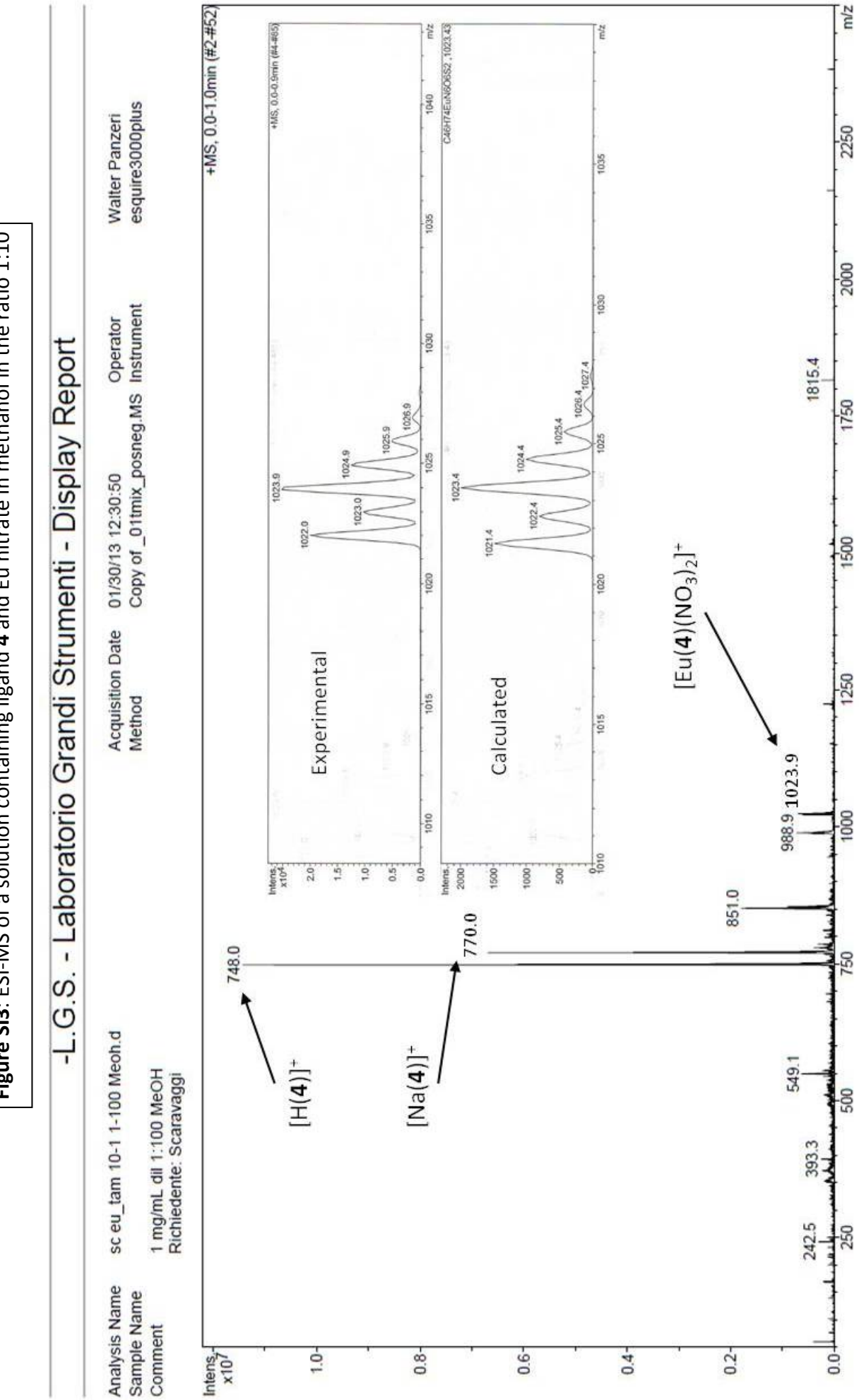

Figure SI4. A view of the optimized structure of the ligand **9** obtained by DFT calculations.

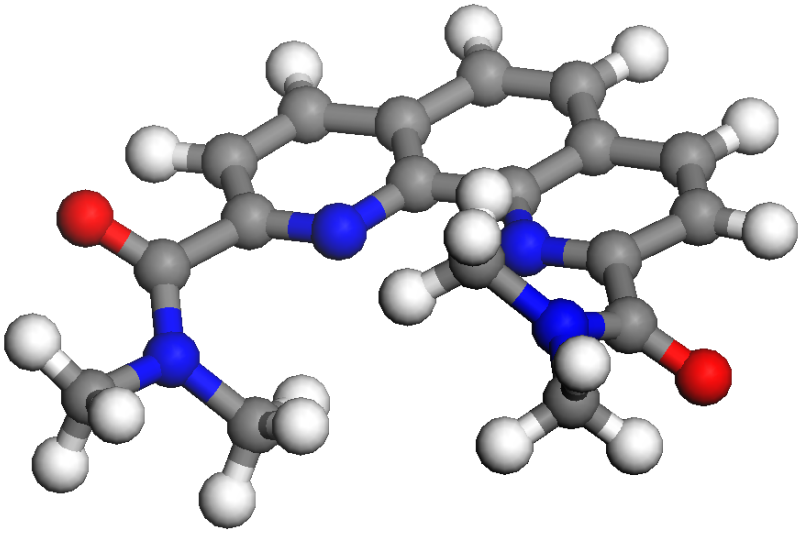

Table SI2: Selection of Eu to O/N atom distances in the $[Eu(\mathbf{9})(NO_3^-)_2]^+$ complex as measured in the DFT minimised structure.

	$[Eu(\mathbf{1})(NO_3^-)_2]^+$
	Bond Length (Å)
$M\text{-}N_{1,2}$	2.62
$M\text{-}O_{1,2}$	2.46
$M\text{-}O_{5,5'}$	2.56
$M\text{-}O_{6,6'}$	2.47

Table SI3: Selection of Eu to O/N atom distances in the $[Eu(\mathbf{9})_2(NO_3^-)]^{2+}$ complex as measured in the DFT minimised structure.

	$[Eu(\mathbf{1})_2(NO_3^-)]^{2+}$
	Bond Length (Å)
$M\text{-}N_{1,2}$	2.68
$M\text{-}O_{1,2}$	2.55
$M\text{-}O_4$	2.41
$M\text{-}O_{5,6}$	2.52
	Non-bonded (Å)
$M\text{-}N_4$	3.39
$M\text{-}N_3$	4.04
$M\text{-}O_3$	4.99