Unusual extraction of trivalent *f*-cations using diglycolamide dendrimers in a room temperature ionic liquid: extraction, spectroscopicand DFT studies

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Electronic Supporting Information

1. Kinetics of extraction studies

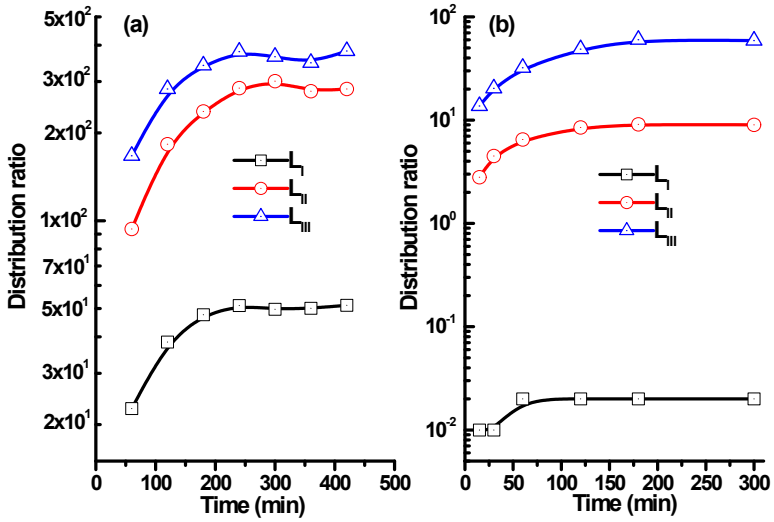

Fig. S1 Kinetics for the extraction of Am^{3+} at (a) 0.1 M HNO_3 and (b) 3 M HNO_3. [L]: 0.1 mmol/L / $[C_4mim][Tf_2N]$.

Table S1 Extraction data and separation factor for Am and Eu by DGA-Dens $\mathbf{L_{I\text{-}III}}$. Ligand: 0.1 mmol/L in $[C_4mim][Tf_2N]$

$[HNO_3]$, M	$\mathbf{L_I}$			$\mathbf{L_{II}}$			$\mathbf{L_{III}}$		
	D_{Am}	D_{Eu}	D_{Eu}/D_{Am}	D_{Am}	D_{Eu}	D_{Eu}/D_{Am}	D_{Am}	D_{Eu}	D_{Eu}/D_{Am}
0.1	52.2	110	2.11	261	455.5	1.75	344	580	1.69
1	1.58	5.62	3.56	41.7	96.5	2.31	92.4	210	2.27
3	0.02	0.11	5.50	9.48	23.35	2.46	52.0	98.7	1.90
4	0.01	0.04	4.00	5.43	14.3	2.63	41.1	73.8	1.80
6	0.01	0.03	3.00	2.83	5.13	1.81	22.3	44.3	1.99

Table S2 *SF* values obtained for the extraction of Am^{3+} with respect to UO_2^{2+}, Cs^+ and Sr^{2+} ions using 1.0 x 10^{-4} M DGA-Dens $\mathbf{L_{I-III}}$ in $[C_4mim][Tf_2N]$. Aqueous phase: 3 M HNO_3

Ligand	*SF* (D_{Am}/D_U)	*SF* (D_{Am}/D_{Cs})	*SF* (D_{Am}/D_{Sr})
$\mathbf{L_I}$	1	190	1733
$\mathbf{L_{II}}$	2	474	5200
$\mathbf{L_{III}}$	0.2	95	520

2. Luminescence spectroscopy of Eu^{3+} ion

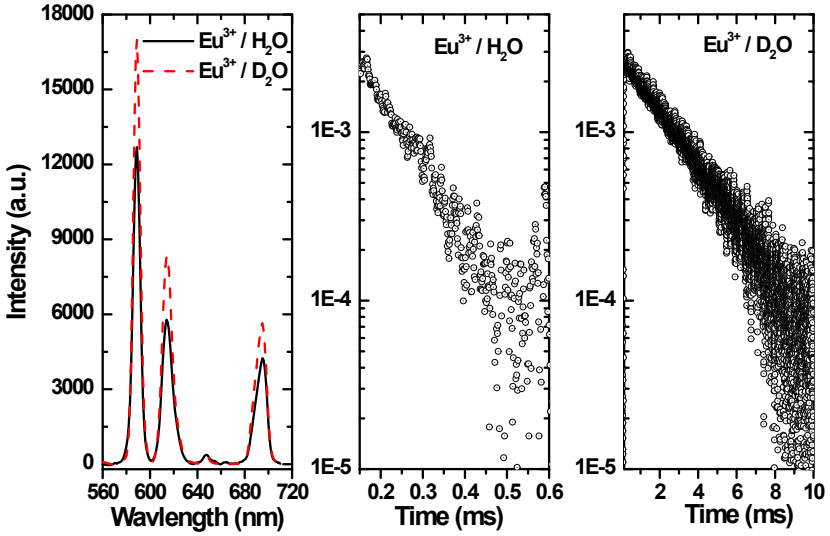

Fig. S2 Emission spectra and fluorescence lifetime of Eu^{3+} in H_2O and D_2O. Excitation: 394 nm; Emission: 614 nm.

3. DFT Studies

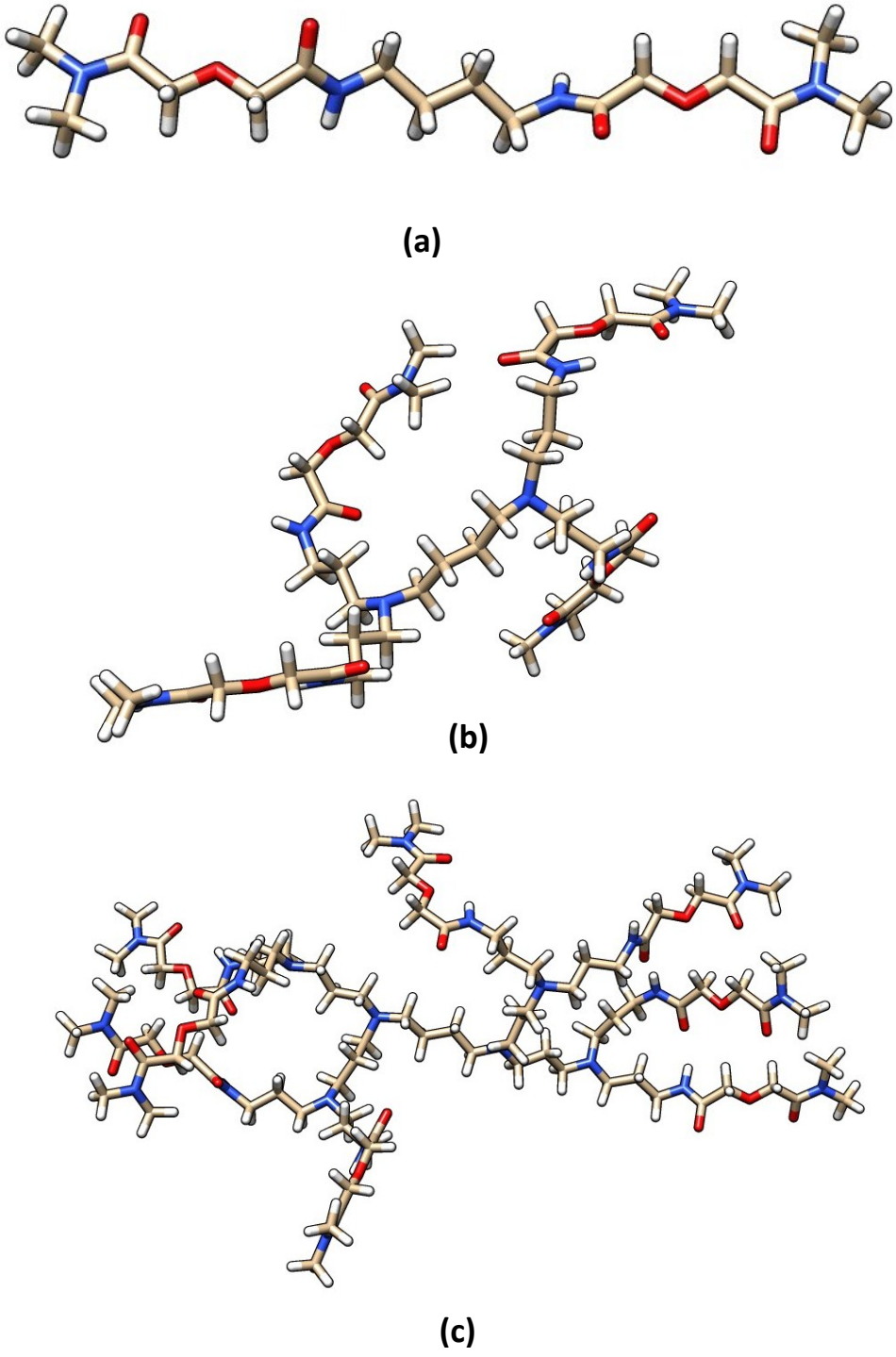

Fig. S3 Optimized structures of (a) $\mathbf{L_I}$, (b) $\mathbf{L_{II}}$ and (c) $\mathbf{L_{III}}$ at the B3LYP/SVP level of theory.

Table S3 Calculated charge and orbital population using NBO analysis in ionic liquid phase at the B3LYP/TZVP level of theory

System	charge	*s*	*p*	*d*	*f*
$(\mathbf{L_I})_2$-$Am^{3+,a}$	2.045	4.14	11.98	10.69	6.13
$(\mathbf{L_I})_2$-$Am^{3+,b}$	2.343	4.10	11.98	10.47	6.09
$\mathbf{L_{II}}$-$[Am^{3+}]_2$	2.289	4.10	11.98	10.51	6.11
	2.298	4.09	11.99	10.49	6.11
$\mathbf{L_{III}}$-$[Am^{3+}]_4$	2.357	4.09	11.98	10.44	6.11
	2.314	4.09	11.98	10.48	6.12
	2.336	4.09	11.98	10.47	6.10
	2.358	4.09	11.98	10.45	6.11

Note: a: Structure given in Fig. 7a; b: Structure given in Fig. 7b

Table S4 Calculated quantum chemical descriptors in the gas phase at the B3LYP/TZVP level of theory

System	$\Delta E_{\text{LUMO-HOMO}}$ (eV)	η(eV)	χ(eV)	ΔN
Am^{3+}-$(H_2O)_9$	3.79	1.89	16.74	
$\mathbf{L_I}$	6.76	3.38	3.26	1.27
$\mathbf{L_{II}}$	5.60	2.80	2.62	1.50
$\mathbf{L_{III}}$	4.64	2.32	3.03	1.62