Electronic Supplementary Material (ESI) for Dalton Transactions.
This journal is © The Royal Society of Chemistry 2016

Benzene-centered tripodal diglycolamides: Synthesis, metal ion extraction, luminescence spectroscopy,and DFT studies

Andrea Leoncini,[a] Seraj Ahmed Ansari,[b] Prasanta Kumar Mohapatra,[b,*] Sheikh Musharaf Ali,[c] Arijit Sengupta,[b] Jurriaan Huskens[a] and Willem Verboom[a,*]

Electronic Supporting Information

Solvent extraction studies

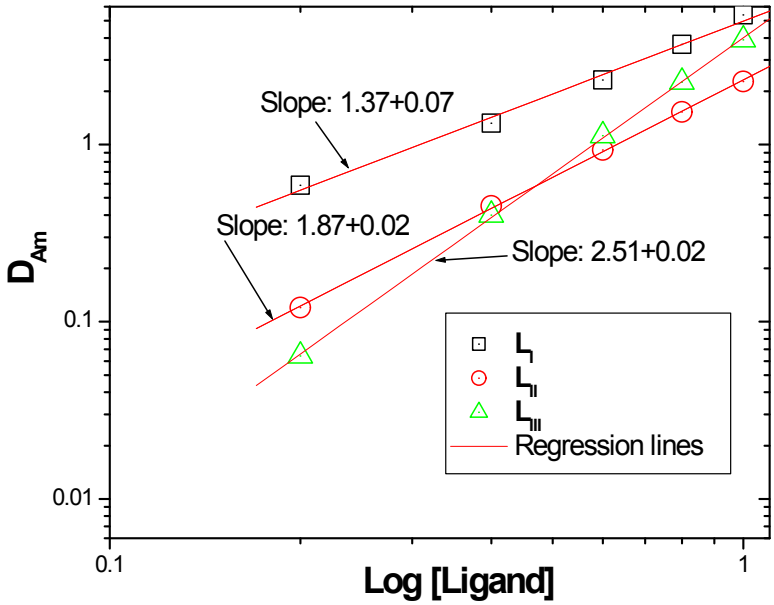

Fig. S1 Extraction of Am(III) with varying concentrations of the Bz-T-DGA ligands $\mathbf{L_I}$, $\mathbf{L_{II}}$, and $\mathbf{L_{III}}$from 1.0 M HNO_3.

Table S1 Distribution measurements (*D*-values) by Bz-T-DGA ligands $\mathbf{L_I}$, $\mathbf{L_{II}}$, and $\mathbf{L_{III}}$ ([ligand]: 1 mmol/L in 95% *n*-dodecane + 5% *iso*-decanol).

$[HNO_3]$ (M)	$\mathbf{L_I}$-Eu	$\mathbf{L_I}$-Am	$\mathbf{L_{II}}$-Eu	$\mathbf{L_{II}}$-Am	$\mathbf{L_{III}}$-Eu	$\mathbf{L_{III}}$-Am
0.1	2.62 ± 0.13	0.10 ± 0.02	1.24 ± 0.05	0.10 ± 0.02	0.12 ± 0.01*	0.007 ± 0.001*
0.2	5.14 ± 0.22	0.22± 0.01	1.62 ± 0.14	0.15± 0.01	0.11 ± 0.05	0.009 ± 0.001
0.5	16.2±1.51	1.14 ± 0.06	3.74 ± 0.24	0.37± 0.02	0.15 ± 0.02	0.014 ± 0.01
1	49.4±2.81	5.22 ± 0.08	10.3±1.3	1.32 ± 0.05	0.34 ± 0.01	0.034 ± 0.01
3	396± 35	235 ± 19.4	110± 5.5	14.3± 0.26	32.7± 1.65	4.06± 0.11
6	670 ± 150	460 ± 110	335± 65	43.0± 1.6	395± 55	61.9± 2.54

*repeat data

Table S2 Separation factor (SF) data obtained by Bz-T-DGA ligands $\mathbf{L_I}$, $\mathbf{L_{II}}$, and $\mathbf{L_{III}}$ ([ligand]: 1 mmol/L in 95% *n*-dodecane + 5% *iso*-decanol).

	SF (Eu/Am)		
$[HNO_3]$ (M)	$\mathbf{L_I}$	$\mathbf{L_{II}}$	$\mathbf{L_{III}}$
0.1	26.2	12.4	16.7
0.2	23.4	10.8	11.7
0.5	14.2	10.1	10.5
1	9.5	7.8	10.0
3	1.7	7.7	8.1
6	1.5	7.8	6.4

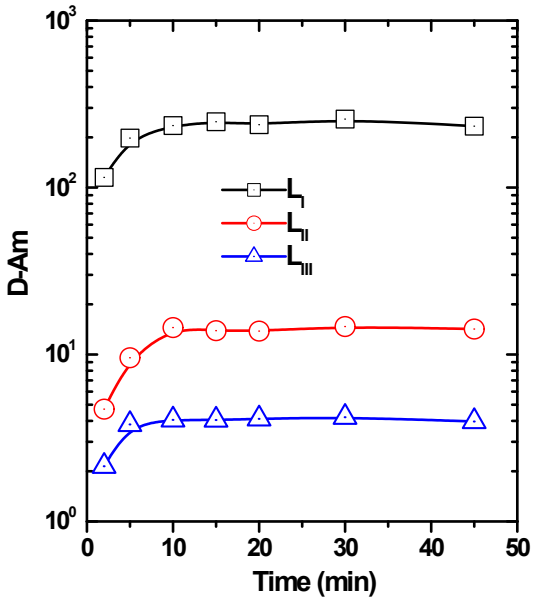

Fig. S2 Kinetics of Am^{3+} ion extraction from 3 M HNO_3; [Ligand]: 1.0 x 10^{-3} M, 95% *n*-dodecane + 5% *iso*-decanol.

Luminescence spectroscopic studies

$I(t) = A_0 + A_1 \exp(-t_1/\tau_1) + A_2 \exp(-t_2/\tau_2) + ...$

$I_{LI}(t) = (8095 \pm 104) \exp(-t/1.33)$ with $\chi^2 = 0.9986$

$I_{LII}(t) = (4543 \pm 116) \exp(-t/1.21)$ with $\chi^2 = 0.9976$

$I_{LIII}(t) = (3500 \pm 117) \exp(-t/0.607)$ with $\chi^2 = 0.9979$

Table S3 Photophysical properties ofthe extracted Eu^{3+} complexes

Photophysical constants	**L_{III}**	**L_{II}**	**L_I**
lifetime (ms)	0.607	1.21	1.33
Number of species	1	1	1
Numberof water molecules	1	0	0
Asymmetry factor	3.90	1.805	2.179
Ω_2 (10^{-20})	6.37	2.94	4.44
Ω_4 (10^{-20})	3.09	1.83	5.23
τ_r (ms)	3.76	6.18	4.34
τ_{nr} (ms)	0.73	1.96	1.92
Quantum efficiency (η)	0.16	0.19	0.31
A_{md} (magnetic dipole transition probability)	42.9	43.2	42.8
A_{2ed} (electric dipole transition probability)	168	78.1	117
A_{4ed} (electric dipole transition probability)	39.7	23.6	67
$\beta 1$ (branching ratio)	0.16	0.26	0.19
$\beta 2$ (branching ratio)	0.63	0.48	0.51
$\beta 4$ (branching ratio)	0.15	0.15	0.29

Computational methods

Table S4 Quantum chemical descriptors of $\mathbf{L_I}$, $\mathbf{L_{II}}$, and $\mathbf{L_{III}}$at the B3LYP/TZVP level of theory

S.No	Complex	E_{HOMO} (eV)	E_{LUMO} (eV)	ΔE (eV)	χ (eV)	η (eV)	ΔN
Gas Phase							
1	$\mathbf{L_I}$	-6.118	-0.374	5.744	3.246	2.872	2.806
2	$\mathbf{L_{II}}$	-6.495	-2.028	4.467	4.261	2.233	3.111
3	$\mathbf{L_{III}}$	-6.042	-0.241	5.801	3.141	2.900	2.801
Solvent Phase							
1	$\mathbf{L_I}$	-6.108	-0.352	5.756	3.23	2.878	0.609
2	$\mathbf{L_{II}}$	-6.536	-1.943	4.593	4.239	2.296	0.574
3	$\mathbf{L_{III}}$	-6.095	-0.26	5.835	3.177	2.917	0.610

Table S5 Orbital occupations of 'Am' with $\mathbf{L_I}$,$\mathbf{L_{II}}$, and $\mathbf{L_{III}}$ at the B3LYP/TZVP level of theory

S.No	Complexation	s	p	d	f
1	$(AmL_I(NO_3)_3)_g$	4.15	11.98	10.70	6.15
2	$(Am(L_{II})_2(NO_3)_3)_g$	4.15	11.98	10.73	6.14
3	$(Am(L_{III})_2(NO_3)_3)_g$	4.15	11.98	10.70	6.16