Electronic Supplementary Information (ESI)

Completely preorganized bis-lactam-1,10-phenanthroline ligands with high stability for efficient separation of Am(III) over Eu(III)

Fengxin Gao,[‡a] Xiaocheng Xu,[‡a] Xiaofan Yang,[a] Hong Cao,[c] Dong Fang,*[b] Lei Xu,[d] Chao Xu*[c] and Chengliang Xiao*[a,b]

a. College of Chemical and Biological Engineering, Zhejiang University, Hangzhou 310058, China

b. Institute of Zhejiang University-Quzhou, Quzhou, 324000, China

c. Institute of Nuclear and New Energy Technology, Tsinghua University, Haidian District, Beijing 100084, China

d. Institute of Nuclear-Agricultural Science, Key Laboratory of Nuclear Agricultural Sciences of Ministry of Agriculture and Zhejiang Province, Zhejiang University, Hangzhou 310058, China

* Corresponding E-mail: xiaoc@zju.edu.cn

‡ These two authors contributed equally to this work.

Content

1. Experimental section

1.1 General

The chemicals and reagents used in this work, such as europium nitrate hexahydrate ($Eu(NO_3)_3·6H_2O$), tetraethylammonium nitrate (Et_4NNO_3), sodium thiosulphate ($Na_2S_2O_3$), acetic acid, 4-tert-butylaniline, potassium carbonate (K_2CO_3), potassium iodide (KI), Br_2, anhydrous magnesium sulfate ($MgSO_4$), $Cy_3P·HBF_4$, cesium carbonate (Cs_2CO_3), $Pd(OAc)_2$, thionyl chloride ($SOCl_2$), deuterated chloroform (CD_3Cl), triethylamine (NEt_3), N, N-dimethylformamide (DMF), dichloromethane (DCM), petroleum ether (PE), methanol (MeOH), dimethyl sulfoxide (DMSO) with analytical purity (AR) are commercially obtained and directly used without purification. 1,2-dichloroethane (1,2-DCE) with AR purity was used as a diluent in solvent extraction. Methanol with HPLC purity and trichloromethane ($CHCl_3$) with AR purity were used as the solvents in spectroscopic titration and ESI-MS.

1.2 Organic synthesis

Synthesis of **1**: A mixture of 4-tert-butylaniline (5.0 g, 33.5 mmol, 2 eq.), bromo-alkanes (25.1 mmol, 1.5 eq), K_2CO_3 (6.9 g, 50.3 mmol, 3 eq.), and KI (0.3 g, 1.6 mmol, 0.1 eq.) in DMF was stirred. The reaction mixture was heated to 80 ℃ for 16 hours. After finishing, the reaction was quenched with water, and the mixture was extracted with PE (15 mL × 3). The combined organic layer was washed with brine, dried over $MgSO_4$, and then concentrated under reduced pressure. The residue was purified via flash column chromatography (DCM: PE, 1:5 to 3:5) to afford intermediate **1**.

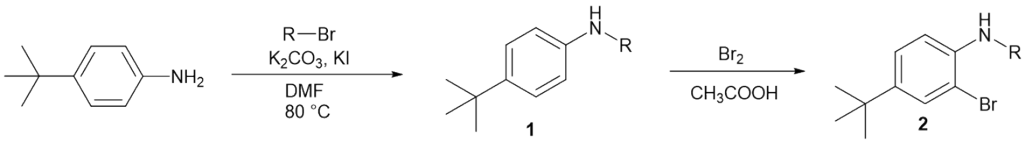
R = n-butyl: Yield: 52%, light yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.24 – 7.17 (m, 2H), 6.61 – 6.51 (m, 2H), 3.10 (t, *J* = 7.0 Hz, 2H), 1.65 – 1.56 (m, 2H), 1.47 – 1.39 (q, *J* = 7.4 Hz, 2H), 1.29 (s, 9H), 0.96 (t, *J* = 7.7 Hz, 3H).

R = 2-ethylhexyl: Yield: 48%, light yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.20 (d, *J* = 8.7 Hz, 2H), 6.57 (d, *J* = 8.7 Hz, 2H), 3.00 (d, *J* = 6.2 Hz, 2H), 1.58 – 1.51 (m, 1H), 1.48 – 1.29 (m, 8H), 1.28 (s, 9H), 0.93 – 0.87 (m, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 146.46, 139.67, 126.01, 112.33, 47.22, 39.22, 33.85, 31.61, 31.39, 29.04, 24.55, 23.18, 14.17, 10.99. m/z calculated for $[C_{18}H_{31}N + H]^+$ 262.2529, found 262.2502.

Synthesis of **2**: The intermediate **1** (3.0 g, 14.6 mmol, 1.0 eq.) was added to 30 mL glacial acetic acid and then the solution was stirred. Bromine (0.5 mL, 1.0 eq.) solution in 15 mL glacial acetic acid was added dropwise over 20 minutes through a dropping funnel. The reaction mixture was stirred at room temperature for 4 hours. After finishing, the reaction was added sodium thiosulphate to quench excess bromine until the solution was colorless. It was diluted with 100 mL water and extracted with DCM (3 × 40 mL). The combined organic layer was washed with brine, dried over $MgSO_4$, and then concentrated under reduced pressure. The residue was purified via flash column chromatography (DCM: PE, 1:5) to afford intermediate **2**.

R = n-butyl: Yield: 82%, light yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.42 (d, J = 2.2 Hz, 1H), 7.19 (dd, J = 8.5, 2.2 Hz, 1H), 6.58 (d, J = 8.5 Hz, 1H), 4.12 (s, 1H), 3.13 (t, J = 7.0 Hz, 2H), 1.68 – 1.59 (m, 2H), 1.49 – 1.40 (m, 2H), 1.26 (s, 9H),0.96 (t, J = 7.4 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 142.86, 140.61, 129.33, 125.28, 110.91, 109.53, 43.72, 33.88, 31.45, 20.29, 13.91. m/z calculated for $[C_{14}H_{22}BrN + H]^+$ 284.1008, found 284.0986.

R = 2-ethylhexyl: Yield: 86%, light yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.43 (s, 1H), 7.19 (d, J = 8.5 Hz, 2H), 6.58 (d, J = 8.5 Hz, 2H), 3.04 (d, J = 6.0 Hz, 2H), 1.64 – 1.58 (m, 1H), 1.48 – 1.29 (m, 8H), 1.27 (s, 9H), 0.95 – 0.88 (m, 7H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 143.02, 140.46, 129.33, 125.31, 110.83, 109.63, 47.08, 38.90, 33.91, 31.48, 31.33, 28.98, 24.59, 23.11, 14.12, 11.00. m/z calculated for $[C_{18}H_{30}NBr + H]^+$ 340.1634, found 340.1581.



Scheme S1 Synthetic routes for **1** and **2**.

1.3 Solvent extraction

The distribution ratio (D) was calculated as equation S1:

$$D = C_{org}/C_{aq} \qquad \text{S1}$$

The separation factor (SF) was calculated as equation S2:

$$SF = D_{Am}/D_{Eu} \qquad \text{S2}$$

2 Result and discussion

2.1 Organic synthesis

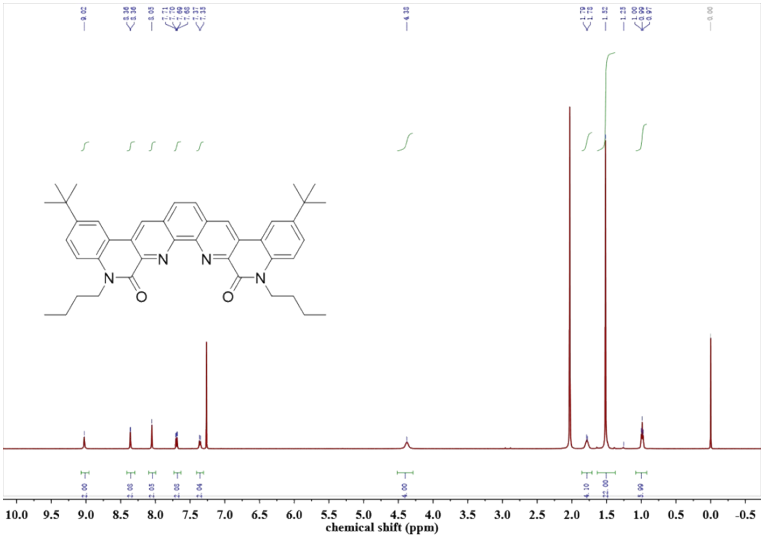


Fig. S1 ^{1}H spectrum of **L1** in $CDCl_3$.

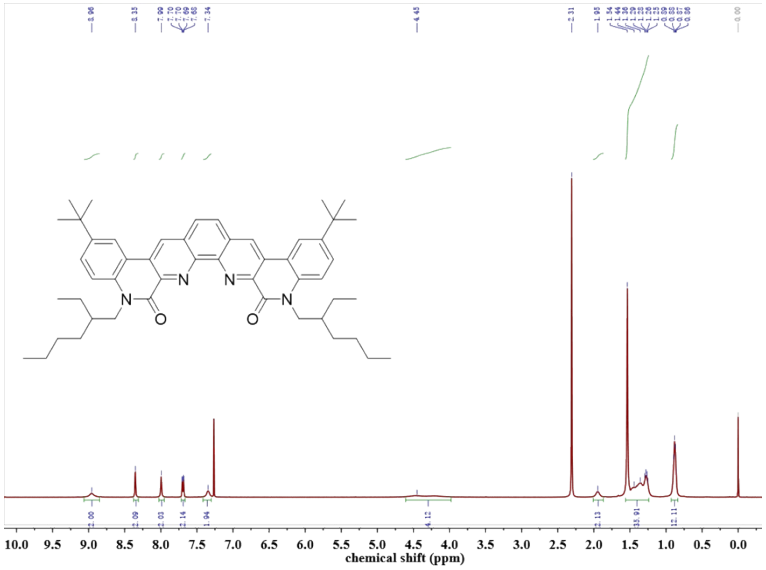


Fig. S2 ^{1}H spectrum of **L2** in $CDCl_3$.

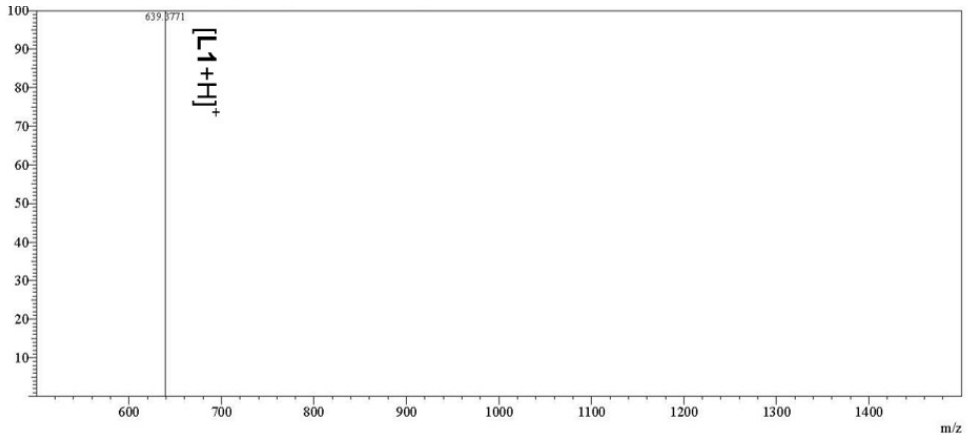


Fig. S3 The ESI-HRMS result of **L1**.

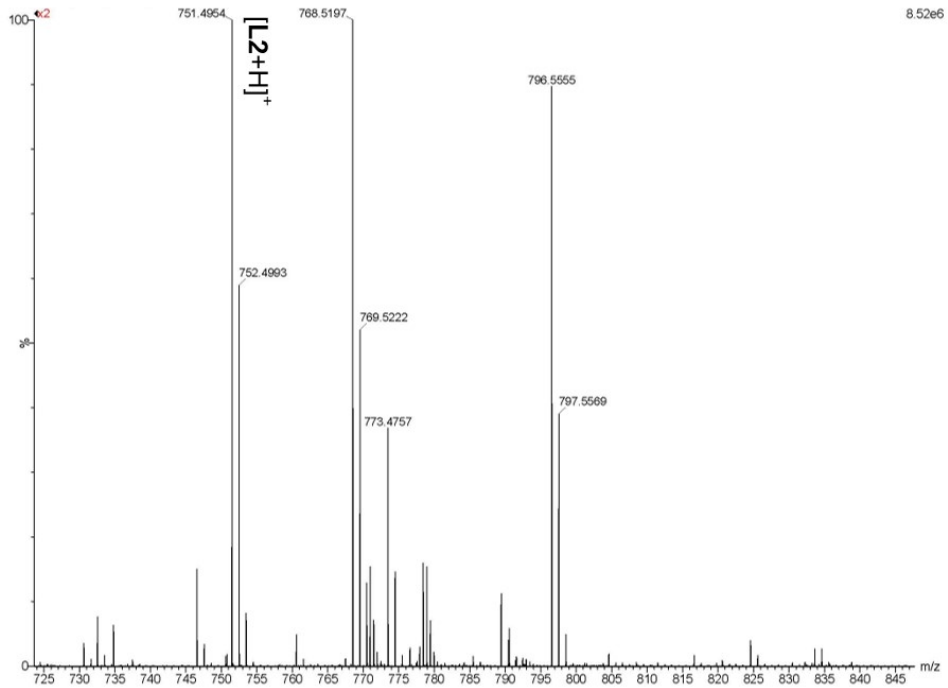


Fig. S4 The ESI-HRMS result of **L2**.

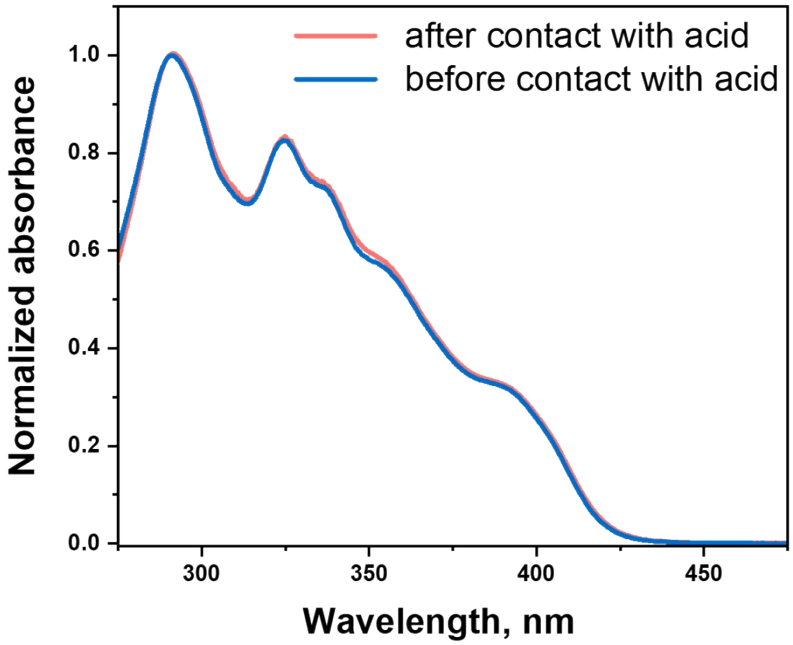


Fig. S5 The UV-Vis absorption spectra of (a) **L1** and (b) **L2** in 1,2-DCE before and after 24 hours of exposure to 1 M nitric acid.

2.2 ESI-MS results

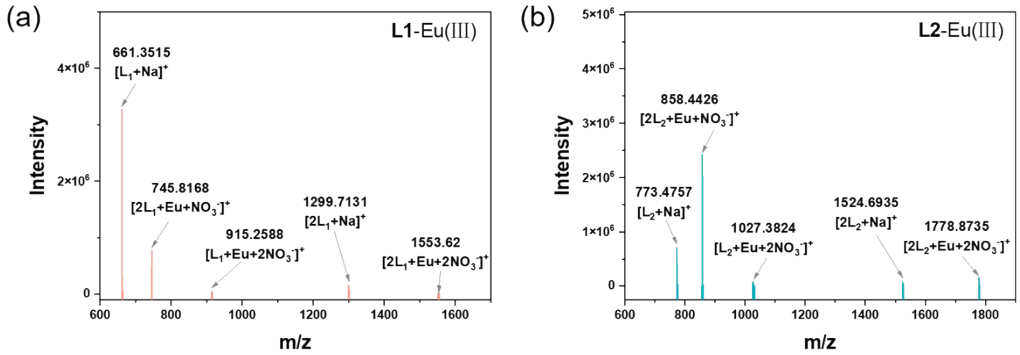


Fig. S6 ESI-MS spectrum of the complex solution.

2.3 Single-crystal X-ray diffraction

Table S1. Structural refinement parameters for **L1**

Identification code	**L1**
CCDC number	2390588

Empirical formula	$C_{44}H_{50}C_{l6}N_4O_3$
Formula weight	895.58
Temperature/K	302.0
Crystal system	monoclinic
Space group	P21/c
a/Å	16.465(10)
b/Å	14.702(12)
c/Å	18.759(12)
α /°	90
β /°	92.77(5)
γ /°	90
Volume/Å3	4536(5)
Z	4
ρ calcg/cm3	1.311
μ /mm-1	3.795
F(000)	1872.0
Crystal size/mm3	0.18 × 0.15 × 0.12
Radiation	CuKα (λ = 1.54178)
2Θ range for data collection/°	7.644 to 137.31
Index ranges	-19 ⩽ h ⩽ 19, -16 ⩽ k ⩽ 17, -22 ⩽ l ⩽ 21
Reflections collected	42015
Independent reflections	8331 [Rint = 0.0905, Rsigma = 0.0629]
Data/restraints/parameters	8331/348/666
Goodness-of-fit on F2	1.058
Final R indexes [I>=2σ (I)]	R1 = 0.0836, wR2 = 0.2380
Final R indexes [all data]	R1 = 0.1262, wR2 = 0.2824
Largest diff. peak/hole / e Å-3	0.47/-0.37

2.4 DFT calculation details

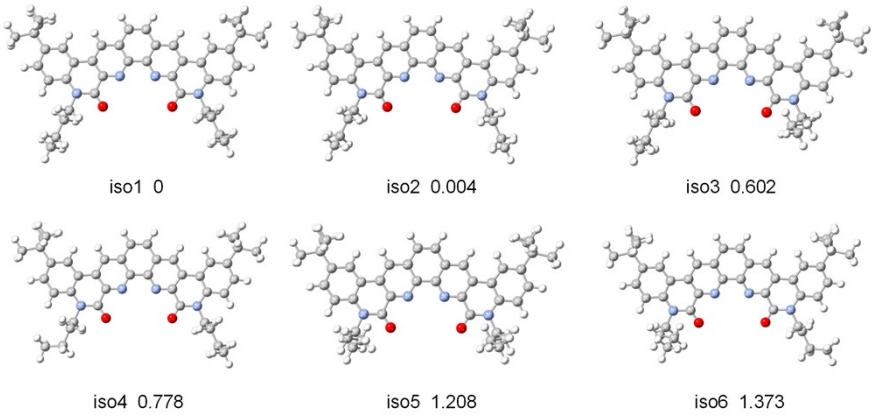


Fig. S7 Six calculated isomers of **L1** (kcal/mol).

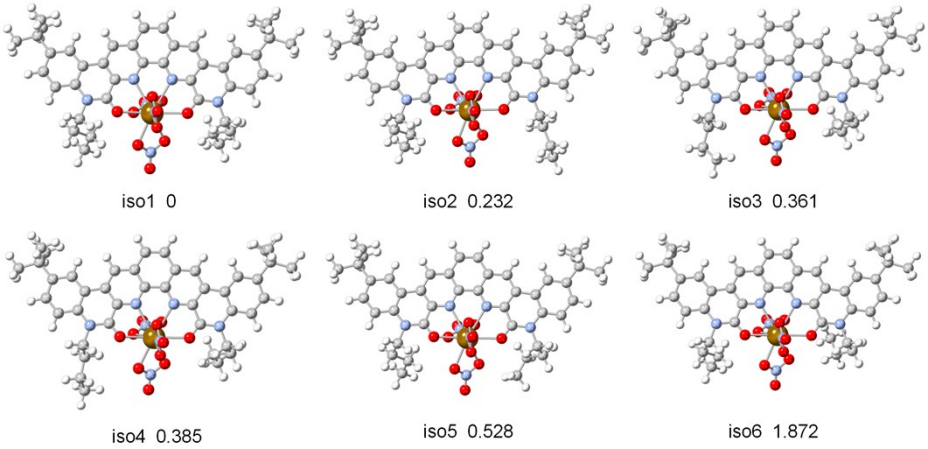


Fig. S8 Six calculated isomers of Eu**L1**$(NO_3)_3$ (kcal/mol).

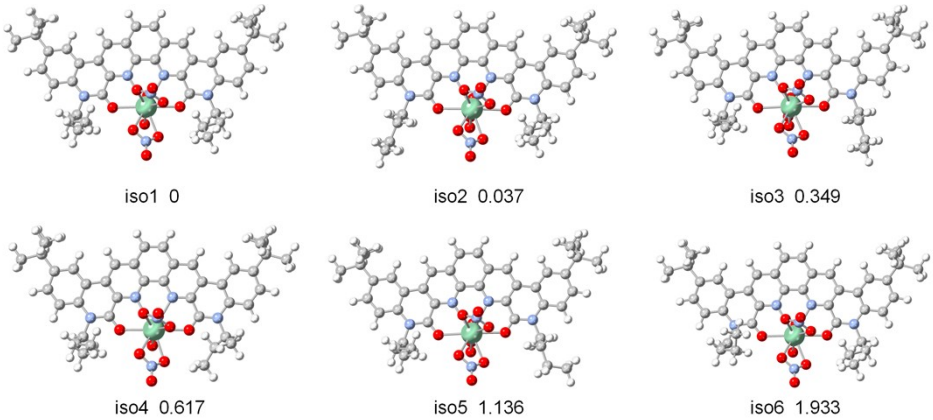


Fig. S9 Six calculated isomers of Am**L1**$(NO_3)_3$ (kcal/mol).

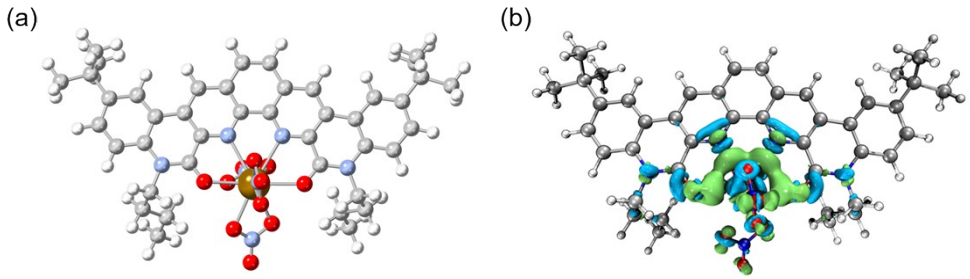


Fig. S10 (a) Optimized structure of Eu(**L1**)$(NO_3)_3$ and (b) deformation density $\Delta\rho$ between **L1** and Eu$(NO_3)_3$ (isosurface = 0.003 a.u.)

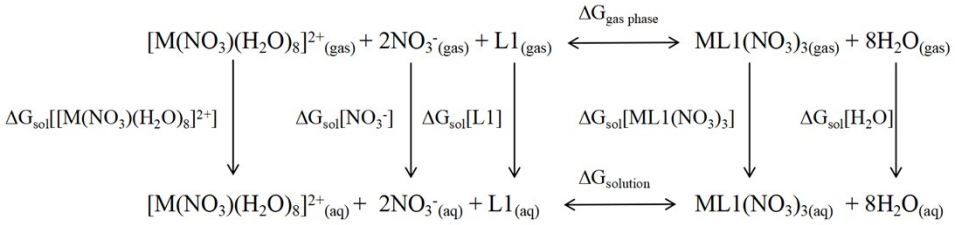
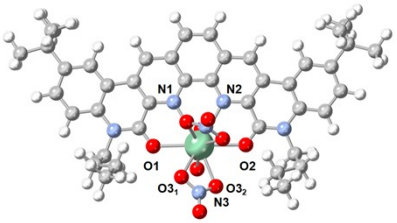


Fig. S11 Thermodynamic cycle for calculating the Gibbs free energy of the reaction.



	Am**L1**$(NO_3)_3$	Eu**L1**$(NO_3)_3$
M-O1	2.526	2.495
M-O2	2.534	2.492
M-N1	2.705	2.725
M-N2	2.679	2.688
M-$O3_1$/$O3_2$	2.501	2.457
M-N3	2.937	2.889
∠$O3_1$-N3-$O3_2$	115.3	115.3

Fig. S12. The bond distances and angles of Am**L1**$(NO_3)_3$ and Eu**L1**$(NO_3)_3$ (distance Å/ angle deg).

Table S2. EDA Analysis (kcal/mol) of M**L1**$(NO_3)_3$ at the PBE0/6-311G* level of theory.

ML1$(NO_3)_3$	E_{int}	E_{elest}	E_{xrep}	E_{orb}	E_c
Am**L1**$(NO_3)_3$	-93.84	-100.00	100.39	-70.05	-24.18
Eu**L1**$(NO_3)_3$	-92.02	-91.72	86.60	-65.30	-21.60

Appendix A

Optimized cartesian coordinates of M**L1**$(NO_3)_3$

Am**L1**$(NO_3)_3$				Eu**L1**$(NO_3)_3$			
Am	-0.01061000	-1.56563311	0.43027403	Eu	-0.02097700	-1.65957812	0.49278504

O	0.09298401	-0.44531103	2.66536519	O	0.01421700	-0.53163604	2.67099219
O	0.27869102	-2.58413019	2.67588619	O	0.33831702	-2.65237419	2.68846819
O	-0.95027207	-3.82901928	0.23992202	O	-1.01476607	-3.87465228	0.35421903
O	0.81627706	-3.46964525	-0.92036606	O	0.84080006	-3.60312926	-0.67857605
O	-1.44587110	-1.49409811	-1.68322612	O	-1.34035010	-1.60144411	-1.62055412
O	0.49619304	-0.59664604	-1.84744013	O	0.64486805	-0.80390606	-1.75864613
N	0.26371902	-1.50848211	3.34497824	N	0.25709402	-1.57803911	3.35296424
N	-0.11866601	-4.27471231	-0.60879505	N	-0.12736601	-4.37892832	-0.39487303
N	-0.59184004	-0.91826307	-2.41964017	N	-0.43598403	-1.09780708	-2.35288117
O	0.40103403	-1.48708310	4.53725733	O	0.39924803	-1.54305811	4.54445333
O	-0.20673701	-5.37156739	-1.08331108	O	-0.19129901	-5.50205340	-0.80952206
O	-0.79857706	-0.67435405	-3.57841526	O	-0.59652504	-0.89854306	-3.52743825
O	2.50027418	-1.59907311	0.70027605	O	2.45996917	-1.66535812	0.75651105
O	-2.47192218	-1.47109810	1.02540308	O	-2.45414118	-1.55823711	1.02123307
N	1.38438710	0.74937505	0.32025302	N	1.36809510	0.68116205	0.36766803
N	-1.29711609	0.78213105	0.32086202	N	-1.29723409	0.70051005	0.33774502
C	3.25402823	-0.64408205	0.50843904	C	3.22276523	-0.72150905	0.55073304
C	-3.19995023	-0.53229904	0.70915505	C	-3.19000923	-0.62541504	0.70675905
C	2.70465119	0.70610005	0.30890702	C	2.68604919	0.63275904	0.34951003
C	0.77867606	1.91178914	0.10911601	C	0.76853806	1.84192813	0.14271201
C	-0.66298405	1.92847614	0.10124701	C	-0.67195305	1.85243313	0.12519801
C	-2.61914919	0.77439805	0.35323703	C	-2.61863419	0.68662405	0.36030003
N	4.60502433	-0.78585405	0.45509003	N	4.57124633	-0.87716106	0.47919403
N	-4.55658733	-0.63548405	0.69752705	N	-4.54518233	-0.74114805	0.68583705
C	3.53296626	1.82308613	0.09486301	C	3.51927225	1.74317513	0.12141101
C	1.49617711	3.11085422	-0.11326601	C	1.48701911	3.03806722	-0.08911501
C	-1.35319710	3.14320722	-0.12252301	C	-1.36616210	3.06314322	-0.10655701
C	-3.42012825	1.90558114	0.11415401	C	-3.42598525	1.81281313	0.11898201
C	5.46936242	0.30051802	0.26236102	C	5.44273041	0.20222001	0.27737802
C	5.12808937	-2.15272515	0.59963904	C	5.08111037	-2.25044016	0.60781205
C	-5.39210540	0.44838703	0.39984703	C	-5.38781340	0.33827302	0.39065503
C	-5.12022237	-1.94933714	1.04504608	C	-5.09841437	-2.06419715	1.01390507
C	2.88898121	3.04102522	-0.11349001	C	2.88035821	2.96365922	-0.09145901
C	0.76280206	4.32580231	-0.33658802	C	0.75008505	4.24980830	-0.31982302
C	-0.59150204	4.34120531	-0.34211802	C	-0.60496504	4.26177530	-0.32738202
C	-2.74709820	3.10270822	-0.12610501	C	-2.75999120	3.01482822	-0.11816201
C	-4.86234635	1.72922813	0.12605001	C	-4.86698935	1.62485812	0.12548801
H	4.33990331	-2.72274420	1.08904708	H	4.29094531	-2.81539020	1.10004608
H	5.97613144	-2.11769915	1.28659009	H	5.93646241	-2.23113416	1.28636409
C	5.49613138	-2.80822020	-0.72743105	C	5.42750439	-2.89766221	-0.72915605
H	-5.95628142	-1.78078213	1.72723812	H	-5.93938040	-1.91304614	1.69413112
H	-4.34368731	-2.46833518	1.60539311	H	-4.31942431	-2.58329219	1.57073212
C	-5.53075941	-2.78521420	-0.16312101	C	-5.49440938	-2.88668721	-0.20826002
H	3.45564825	3.94888229	-0.29157702	H	3.45068225	3.86771728	-0.27755902
H	1.31961810	5.24239738	-0.50689304	H	1.30369909	5.16762937	-0.49428504
H	-1.12619108	5.27019638	-0.51609504	H	-1.14057508	5.18927438	-0.50669204
H	-3.29339524	4.02109129	-0.31376002	H	-3.31135624	3.92921028	-0.31074502
H	6.29213144	-2.24181216	-1.22697709	H	6.22188945	-2.33309517	-1.23347509
H	5.92888443	-3.78680627	-0.48342303	H	5.85531043	-3.88178728	-0.49902604
H	-6.27280043	-2.24716816	-0.76659306	H	-6.23925345	-2.34760617	-0.80735806
C	4.97067536	1.61152511	0.09486701	C	4.95502636	1.51834011	0.11246301
C	5.87632941	2.66298619	-0.07224201	C	5.86905042	2.56105918	-0.06293300
C	6.85298047	0.11233501	0.23865202	C	6.82435648	0.00174300	0.24222902
C	7.71688154	1.17991809	0.06913600	C	7.69678556	1.06112807	0.06454300
C	7.25317453	2.48818218	-0.08893301	C	7.24409051	2.37353417	-0.09071801
H	5.47932137	3.66527526	-0.19082601	H	5.47980340	3.56678226	-0.17891201
H	7.27422652	-0.87745306	0.34878403	H	7.23717654	-0.99185007	0.35020603
H	8.78036662	0.97209207	0.06085600	H	8.75818865	0.84333706	0.04777700
C	-5.74140143	2.78300220	-0.13950001	C	-5.75356642	2.67316919	-0.13647601
C	-6.78011049	0.29209802	0.38253203	C	-6.77446851	0.17140901	0.36803203
C	-7.61712152	1.36110110	0.11541601	C	-7.61904455	1.23533909	0.10430101
C	-7.12179749	2.63964419	-0.15226901	C	-7.13282052	2.51921118	-0.15422701
H	-5.31972040	3.75975427	-0.35035203	H	-5.33874136	3.65458626	-0.33923902
H	-7.22495054	-0.67546005	0.56984104	H	-7.21231754	-0.80051906	0.54922704
H	-8.68513065	1.17752508	0.11453201	H	-8.68559262	1.04351108	0.09932201
C	8.18117557	3.68783526	-0.27419802	C	8.18165157	3.56437426	-0.28452402
C	-8.01939556	3.83878828	-0.45425703	C	-8.03879356	3.71336427	-0.45096003

C	7.87789055	4.36614331	-1.61736711	C	7.87365157	4.24463431	-1.62562612
H	6.84809850	4.73011534	-1.67045812	H	6.84682149	4.61796333	-1.67046112
H	8.53804059	5.22623237	-1.76695813	H	8.54044062	5.09852837	-1.78130913
H	8.02870760	3.67526427	-2.45157217	H	8.01118559	3.55178625	-2.46050118
C	9.65432672	3.27972024	-0.26642202	C	9.65097671	3.14262422	-0.28864302
H	10.28174572	4.16496330	-0.40110503	H	10.28548574	4.02190629	-0.42918703
H	9.94705371	2.81533820	0.68002305	H	9.94715473	2.67612719	0.65568705
H	9.89283071	2.58626818	-1.07840908	H	9.87624069	2.44637918	-1.10201908
C	7.95417960	4.68936734	0.86668306	C	7.97348557	4.56878933	0.85740406
H	8.61436362	5.55457138	0.75042806	H	8.64071463	5.42775840	0.73508305
H	6.92618849	5.06160536	0.88789106	H	6.94917950	4.95050136	0.88683306
H	8.16207656	4.23388930	1.83897113	H	8.18516758	4.11197330	1.82825313
C	-7.69302057	4.38228932	-1.85218413	C	-7.71228855	4.26909531	-1.84403513
H	-8.33155462	5.24005738	-2.08574015	H	-8.35665260	5.12357037	-2.07362715
H	-6.65444650	4.71522734	-1.93130114	H	-6.67606848	4.61055033	-1.91752414
H	-7.85589455	3.62054226	-2.61969419	H	-7.86698055	3.51150125	-2.61734419
C	-9.50205866	3.46814325	-0.41941603	C	-9.51862567	3.33098424	-0.42343803
H	-9.81010973	3.09839222	0.56320904	H	-9.82699170	2.95256121	0.55577504
H	10.10728270	4.35213631	-0.63802605	H	-10.13003071	4.21162130	-0.63838304
H	-9.75351671	2.70975020	-1.16681609	H	-9.76169768	2.57542418	-1.17647108
C	-7.77443258	4.93620435	0.59062304	C	-7.80565854	4.80542534	0.60221704
H	-6.73784346	5.28447638	0.58495704	H	-6.77180548	5.16176737	0.60221604
H	-8.41277561	5.80235244	0.38984503	H	-8.45016060	5.66792840	0.40543603
H	-7.99844458	4.57784333	1.59933511	H	-8.02994159	4.43832632	1.60771712
H	-6.04669644	-3.67044627	0.23123902	H	-6.00254543	-3.78322827	0.17021001
C	4.32294931	-2.99527222	-1.68330512	C	4.24085330	-3.06736922	-1.67183012
H	3.51345725	-3.53829226	-1.18625608	H	3.43575025	-3.61363326	-1.17107908
H	3.89909328	-2.01988614	-1.95027614	H	3.81696428	-2.08748915	-1.92158014
C	4.72820034	-3.72460027	-2.95465221	C	4.62769333	-3.78225827	-2.95715221
H	5.11897637	-4.72349034	-2.73452620	H	5.01575236	-4.78597534	-2.75469520
H	3.87204828	-3.84798928	-3.62171726	H	3.76362427	-3.89250728	-3.61634826
H	5.50372438	-3.18030323	-3.50475125	H	5.39963638	-3.23475923	-3.50921025
C	-4.36982031	-3.22530523	-1.04777408	C	-4.32432531	-3.30156124	-1.09318708
H	-3.85153828	-2.35411417	-1.46089611	H	-3.81078727	-2.41900217	-1.48824811
H	-3.62042426	-3.74785827	-0.44457203	H	-3.57385126	-3.82734327	-0.49420004
C	-4.82705035	-4.11975530	-2.18948216	C	-4.76771334	-4.17964630	-2.25296616
H	-3.97874929	-4.42274132	-2.80752520	H	-3.91428828	-4.46240632	-2.87355620
H	-5.30683139	-5.03202636	-1.81882713	H	-5.23912638	-5.10352037	-1.90090214
H	-5.54527242	-3.60951126	-2.84090920	H	-5.48907141	-3.66522127	-2.89766021