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Complexation Thermodynamics of Tetraalkyl Diglycolamides with Trivalent *f*-elements in Ionic Liquid: Spectroscopic, Microcalorimetric and Computational Studies

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Supporting Information

UV-Vis Spectroscopic Measurements

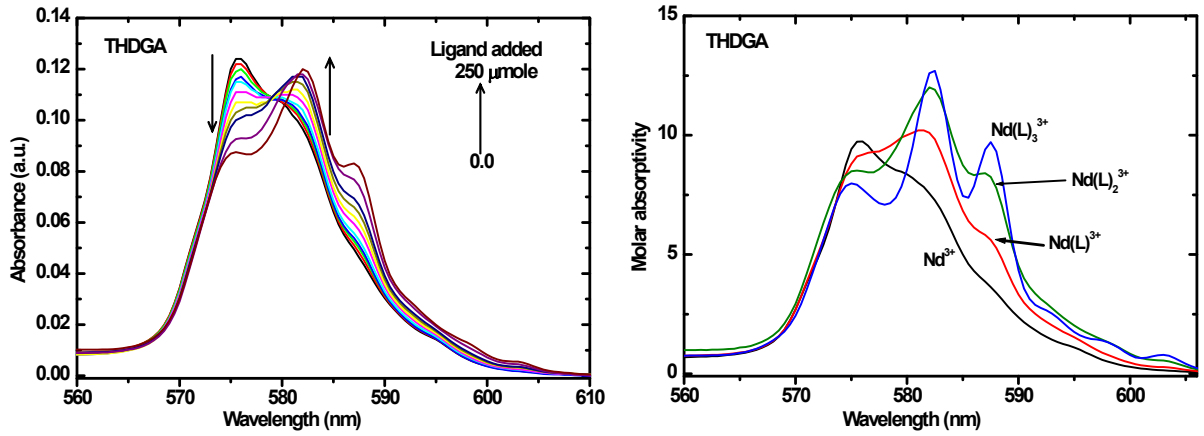

Figure S1. Spectrophotometric titrations of Nd^{3+} with THDGA in $[C_4mim][Tf_2N]$ (left), and deconvoluted spectra of Nd^{3+}, $Nd(L)^{3+}$, $Nd(L)_2{}^{3+}$ and $Nd(L)_3{}^{3+}$ species (right). Cuvette: 25 µmole $Nd(Tf_2N)_3$ (2 mL); Titrant: 100 µmole/mL ligand in $[C_4mim][Tf_2N]$; Temperature: 25°C.

Complexation equilibria:

For ML^{3+} species:

$$M^{3+} + L \rightarrow ML^{3+} \qquad (1)$$

For $ML_2{}^{3+}$ species:

$$M^{3+} + 2L \rightarrow ML_2{}^{3+} \qquad (2)$$

For $ML_3{}^{3+}$ species:

$$M^{3+} + 3L \rightarrow ML_3{}^{3+} \qquad (3)$$

Where M = Nd, Eu or Am as indicated in Table 1 or Table 2.

Luminescence spectroscopy

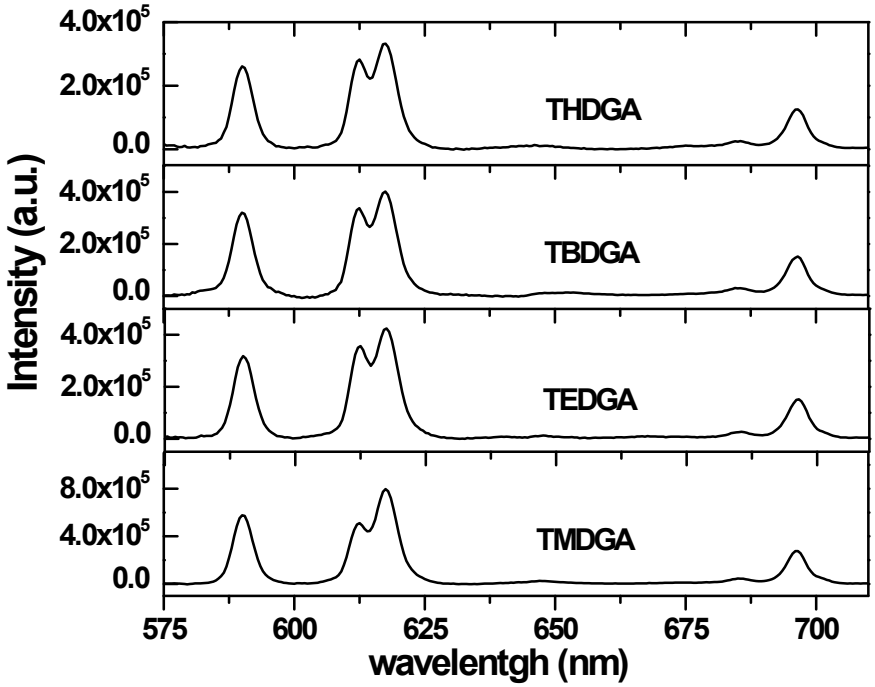

Figure S2. Emission spectra of EuL_3 complex obtained in $[C_4mim][Tf_2N]$.

DFT Calculations

Table S1. Calculated values of binding energies and free energies of extraction (kcal/mol) (1:3 stoichiometry) at the B3LYP level of theory using the TZVP basis set.

Stoichiometric ratio	Δ*G* (kJ/mol)			
	Gas	*n*-dodecane	Ionic liquid	water
1:1	-1612.76	-902.524	-296.24	82.9949
1:2	-2317.76	-1322.66	-401.777	240.6898
1:3	-2576.27	-1454.51	-447.957	243.8271

Table S2. Calculated charges and orbital populations using NBO analysis in the gas phase at the B3LYP/TZVP level of theory.

Phase	System	charge	*s*	*p*	*D*	*f*
Gas	1:1	2.404	4.01	11.97	10.46	3.14
	1:2	2.153	4.07	11.97	10.67	3.12
	1:3	1.911	4.13	11.98	10.83	3.13
n-Dodecane	1:1	2.517	4.01	11.97	10.37	3.11
	1:2	2.184	4.07	11.97	10.64	3.11
	1:3	1.909	4.13	11.98	10.83	3.13
Ionic liquid	1:1	2.592	4.01	11.97	10.32	3.09
	1:2	2.189	4.07	11.97	10.64	3.11
	1:3	1.909	4.13	11.98	10.83	3.13
Water	1:1	2.652	4.00	11.97	10.27	3.08
	1:2	2.196	4.07	11.97	10.63	3.11
	1:3	1.905	4.13	11.98	10.83	3.13

Optimized coordinates of the chemical species

TMDGA

29

Energy = -648.7910720318

H	-5.7956530	-3.4530198	0.4807685
C	-5.5289465	-2.3865700	0.3608759
N	-5.1921889	-1.7857946	1.6395467
C	-4.0890922	-2.4000932	2.3492235
H	-4.3416480	-3.4195787	2.7004338
C	-5.9857313	-0.7616903	2.1184099
O	-6.9301369	-0.3186281	1.4987976
C	-5.6098256	-0.2063694	3.5029687
O	-6.4257693	0.8826413	3.7978412
C	-6.1756515	1.4204992	5.0575689
C	-7.0521866	2.6686208	5.2593614
N	-6.9246801	3.3072226	6.4774513
C	-6.0957040	2.8603257	7.5781475
H	-6.6983854	2.4279188	8.4007237
O	-7.7991893	3.0604615	4.3873091
C	-7.7574882	4.4665125	6.7454560
H	-8.4493809	4.2732179	7.5860644
H	-5.1055350	1.7045366	5.1699222
H	-6.3875876	0.6813264	5.8612719
H	-4.5374325	0.0867605	3.5147232
H	-5.7196153	-1.0164768	4.2586735
H	-4.6748342	-2.3241679	-0.3372997
H	-6.3844703	-1.8474243	-0.0622758
H	-3.7805859	-1.8091328	3.2192307
H	-3.2114266	-2.4890779	1.6842577
H	-8.3410513	4.6909974	5.8449345

H -7.1364007 5.3417852 7.0079770

H -5.5302024 3.7117827 7.9967472

H -5.3638953 2.1077396 7.2625119

Nd^{3+}-TMDGA

30

Energy = -1209.279436520

H -6.2128427 -3.2378715 0.4042923

C -5.7839253 -2.2289764 0.3036105

N -5.2800832 -1.7990120 1.6296161

C -4.2093890 -2.6539346 2.1871895

H -4.5877453 -3.6851102 2.2614398

C -5.7531221 -0.7558432 2.2426185

O -6.7055804 -0.0153755 1.7371754

C -5.2523269 -0.2863058 3.6079834

O -6.0616800 0.8678827 3.9444544

C -5.8555267 1.4324047 5.2636189

C -6.8991468 2.5396042 5.4030524

N -7.0216224 3.2764716 6.4657684

C -6.1749540 3.1160858 7.6680639

H -6.8106011 2.7912747 8.5067644

O -7.6722427 2.6795828 4.3573246

C -8.0436514 4.3447633 6.5697233

H -8.6626249 4.1474450 7.4578296

Nd -7.7708053 1.7102529 2.4443508

H -4.8286587 1.8303232 5.3420342

H -5.9974784 0.6488500 6.0285998

H -4.1871199 0.0018352 3.5697049

H -5.3865702 -1.0667824 4.3771224

H -4.9330975 -2.2720176 -0.3931406

H -6.5400589 -1.5314229 -0.0672994

H -3.8832430 -2.3155174 3.1768509

H	-3.3519864	-2.6410754	1.4966545
H	-8.6679814	4.3709148	5.6724159
H	-7.5277474	5.3082648	6.7023983
H	-5.7336094	4.0927065	7.9180683
H	-5.3707166	2.3881650	7.5131778

Nd^{3+}-$(TMDGA)_2$

59

Energy = -1858.383729675

H	-1.0499873	8.2442687	13.2714537
C	-0.5855539	7.4655929	12.6473885
N	-1.5701890	6.9864860	11.6628608
C	-2.0868529	8.0233209	10.7565729
H	-2.5352544	8.8336616	11.3512913
C	-1.9330077	5.7211712	11.6220368
O	-1.4661554	4.8406244	12.4150635
C	-2.9598735	5.2402792	10.5926745
O	-3.1206139	3.8365960	10.8067705
C	-4.0819030	3.1921985	9.9705625
C	-4.1031430	1.7188051	10.3872557
N	-4.9135099	0.8698440	9.7885691
C	-5.8376699	1.2339277	8.7033867
H	-6.8738269	1.0529869	9.0288497
O	-3.3114731	1.3758865	11.3243298
C	-4.9562412	-0.5483326	10.1805084
H	-5.9832915	-0.8081617	10.4788379
Nd	-1.7836364	2.5679441	12.5721673
H	-3.7946374	3.2957807	8.9087718
H	-5.0766496	3.6532921	10.1068100
H	-2.6068334	5.4312595	9.5635324
H	-3.9252063	5.7594815	10.7302776
H	0.2719566	7.9050627	12.1153798
H	-0.2491020	6.6370892	13.2768241

H	-2.8452299	7.6340347	10.0688684
H	-1.2548312	8.4414144	10.1691836
H	-4.2701470	-0.7287301	11.0127849
H	-4.6716742	-1.1712732	9.3186326
H	-5.6322461	0.6008137	7.8268303
H	-5.7383220	2.2835361	8.4067259
H	2.4793401	0.2528341	9.5665213
C	2.4659166	1.0756904	10.2977956
N	2.1398300	0.5375736	11.6287657
C	3.1195445	-0.4225040	12.1596157
H	3.2465767	-1.2431781	11.4375518
C	1.0516272	0.9152972	12.2681115
O	0.2188753	1.7476165	11.7827840
C	0.7398403	0.3574961	13.6603788
O	-0.4851420	0.9632504	14.0741966
C	-0.9269398	0.6304162	15.3913325
C	-2.1994127	1.4450066	15.6418631
N	-2.8494465	1.3371499	16.7822219
C	-2.4394525	0.4562103	17.8866715
H	-3.2251483	-0.2938435	18.0660743
O	-2.5775587	2.2142775	14.6996928
C	-4.0730199	2.1154693	17.0382781
H	-4.8970706	1.4239936	17.2703861
H	-0.1470707	0.8866861	16.1308624
H	-1.1310508	-0.4526929	15.4634284
H	1.5482661	0.6064670	14.3710667
H	0.6313722	-0.7415732	13.6295039
H	3.4661764	1.5331050	10.3314456
H	1.7247444	1.8240527	10.0032038
H	2.8066554	-0.8480756	13.1190323
H	4.0907121	0.0791325	12.2921786
H	-4.3265790	2.7170841	16.1610212
H	-3.9082071	2.7719020	17.9062348

H	-2.3153225	1.0566003	18.8006530
H	-1.4966786	-0.0606171	17.6775990

Nd^{3+}-$(TMDGA)_3$

88

Energy = -2507.331648726

Nd	0.0183902	-0.0092351	0.0494599
O	-0.6038727	-1.7735396	1.6101156
O	-1.6239342	0.7917127	-1.5845230
O	0.1674547	-1.8355548	-1.5748373
O	2.1461550	-1.5877205	0.0230268
O	1.5383407	1.0653251	-1.5343712
O	-1.2083750	1.3504383	1.6607591
O	0.2897410	2.6351092	0.0398583
O	-2.4339801	-1.0497842	-0.0102289
C	-2.7906580	0.4166043	-1.8423183
C	-1.6844881	-2.3740742	1.8101402
N	-1.8470785	-3.2738097	2.7803095
C	-0.7468834	-3.5859282	3.6975341
H	0.0865184	-2.8990994	3.5206679
H	-1.0963009	-3.4831719	4.7364280
H	-0.4129349	-4.6249807	3.5449836
C	-3.0851967	-4.0178896	3.0273753
H	-3.8358098	-3.8439528	2.2491972
H	-3.5134319	-3.7316687	4.0016246
C	-2.8631243	-2.0556626	0.8878299
H	-3.7332121	-1.7069586	1.4746557
H	-3.1712450	-2.9626564	0.3338580
H	-4.3181360	-0.3009102	-0.4686673
C	-3.4054500	-0.6771182	-0.9678282
H	-3.6936654	-1.5488383	-1.5841824
N	-3.5184278	0.9295106	-2.8356070
C	-4.8994666	0.5441411	-3.1405451

H	-4.9851514	0.3078307	-4.2122610
H	-5.2201137	-0.3358083	-2.5729415
H	-5.5848107	1.3779390	-2.9168922
C	-2.9712302	1.9849753	-3.6916897
H	-3.6049546	2.8835986	-3.6256910
H	-2.9590176	1.6452262	-4.7392380
H	-1.9525306	2.2242915	-3.3723358
C	2.3196103	-2.6348860	-0.9131089
C	1.0719375	-2.6731150	-1.7966059
N	0.9937815	-3.5940801	-2.7581285
C	-0.1909816	-3.6764963	-3.6167263
C	2.0213948	-4.6037964	-3.0294396
H	-0.9215006	-2.9232267	-3.3070145
H	-0.6344917	-4.6818867	-3.5401226
H	0.0956066	-3.5023942	-4.6659313
H	2.2618819	-4.5994388	-4.1035111
H	2.9465535	-4.4147795	-2.4747536
H	1.6488780	-5.6067839	-2.7646786
H	2.4522504	-3.6011487	-0.3917631
H	3.2219225	-2.4566523	-1.5271292
C	1.7529876	2.2718614	-1.7930084
N	2.5440189	2.6740076	-2.7883906
C	3.2185608	1.6950576	-3.6455617
H	2.8922663	1.8266417	-4.6893589
H	2.9735252	0.6829911	-3.3098795
H	4.3079856	1.8506087	-3.6002238
C	2.8410000	4.0748141	-3.1019258
H	2.6574121	4.2567486	-4.1718961
H	2.2189588	4.7696262	-2.5276025
H	3.9004834	4.2943799	-2.8924989
C	1.0742036	3.3241712	-0.9147173
H	1.8332540	3.9527112	-0.4125410
H	4.1653783	-1.2090412	0.3337579

H	3.4099572	-2.3388079	1.4940532
C	3.2412948	-1.4186980	0.9044664
C	2.9090379	-0.2436361	1.8263418
N	3.7847411	0.1040620	2.7697542
C	5.0776191	-0.5508556	2.9885770
C	3.4934323	1.2127948	3.6832782
H	5.3045125	-1.2912342	2.2140176
H	5.0894752	-1.0515993	3.9700535
H	5.8766557	0.2069750	2.9802515
H	2.4669770	1.5587785	3.5273127
H	4.1980894	2.0412246	3.5055146
H	3.6139123	0.8720806	4.7231221
H	-1.0643359	4.1733102	0.3855881
C	-0.4014953	3.4814990	0.9388354
H	0.3119959	4.0921561	1.5223811
C	-1.2277981	2.5861877	1.8646478
N	-1.9395581	3.1504473	2.8406445
C	-2.7262349	2.3234871	3.7604720
C	-2.0209237	4.5932611	3.0853727
H	-1.5253564	5.1757722	2.3014360
H	-3.0785792	4.8976877	3.1192144
H	-1.5609026	4.8425561	4.0552240
H	-2.4867973	2.6024888	4.7978987
H	-2.4890633	1.2670812	3.6004760
H	-3.8024580	2.4937825	3.5944666
O	1.8216204	0.3524707	1.6506915
H	-2.8640797	-5.0962578	3.0534713
H	0.4382646	3.9887515	-1.5284694