

Electronic Supplementary Information

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Title: Structural and photophysical properties of Tb³⁺-tetra-1,3-diketonate complexes controlled by calix[4]arene-tetrathiacalix[4]arene scaffolds

Author(s): Sergey N. Podyachev^{a*}, Svetlana N. Sudakova^a, Rinas N. Nagimov,^b Dmitry V. Lapaev^c, Alexey N. Masliy^b, Victor V. Syakaev^a, Olga B. Bazanova^a, Gulnaz Sh. Gimazetdinova^b, Vasiliy M. Babaev^a, Andrey M. Kuznetsov^b, Asiya R. Mustafina^a

^a*Arbuzov Institute of Organic and Physical Chemistry, FRC Kazan Scientific Center of RAS, Arbuzov str., 8, 420088, Kazan, Russian Federation*

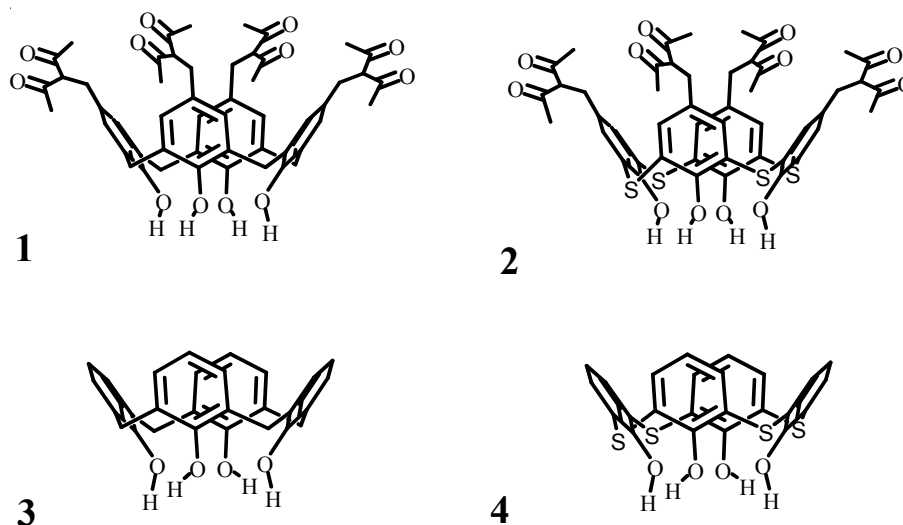
^b*Kazan National Research Technological University, K. Marks Str., 68, 420015, Kazan, Russian Federation*

^c*Zavoisky Physical-Technical Institute, FRC Kazan Scientific Center of RAS, Sibirsky tract, 10/7, 420029, Kazan, Russian Federation*

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1. Structural formulae of the investigated compounds 1-4



Scheme S1. Structural formulae of the compounds 1-4.

2. UV spectral data for compounds 1-4 and their Tb³⁺ complexes

Table S1. UV-spectral data for compounds 1-4 after addition of TEA and/or Tb³⁺ to their DMF solutions ($C_L=0.1$ mM; $C_{TbNO_3^{3+}}=0.1$ mM; $C_{TEA}=0.8$ mM).

Compound	$\lambda_{max}(nm)/$ ($\epsilon_{max}(M^{-1}cm^{-1})$)	Compound	$\lambda_{max}(nm)$ ($\epsilon_{max}(M^{-1}cm^{-1})$)
1	283 (15600) 288 (15800) 308 (7000) sh	3	275 (9200) 282 (9000) 311 (700)
1-Tb³⁺ (1:1)	282 (15200) 289 (15400) 308 (7000) sh	3-Tb³⁺	275 (9200) 282 (9000) 311(700)
1-TEA (1:8)	293 (18000)	3-TEA (1:8)	285(14100) 309 (4600) sh
1-Tb³⁺-TEA (1:1:8)	298 (29400) 305 (30100) 326 (11500) sh	3-Tb³⁺-TEA (1:1:8)	286 (13200) 302 (6300) sh
2	301 (25400) 342 (3600) sh	4	293 (16800) 301 (17800) 335 (3000) sh
2-Tb³⁺ (1:1)	299 (25800) 343 (3900) sh	4-Tb³⁺	293 (16100) 301 (17200) 332 (3700) sh
2-TEA (1:8)	308 (26200) 340 (7800) sh	4-TEA (1:8)	303 (21400) 339 (7800) sh
2-Tb³⁺-TEA (1:1:8)	313 (23300)	4-Tb³⁺-TEA (1:1:8)	314(19000)

3. NMR spectra of the L-Ln³⁺-TEA system.

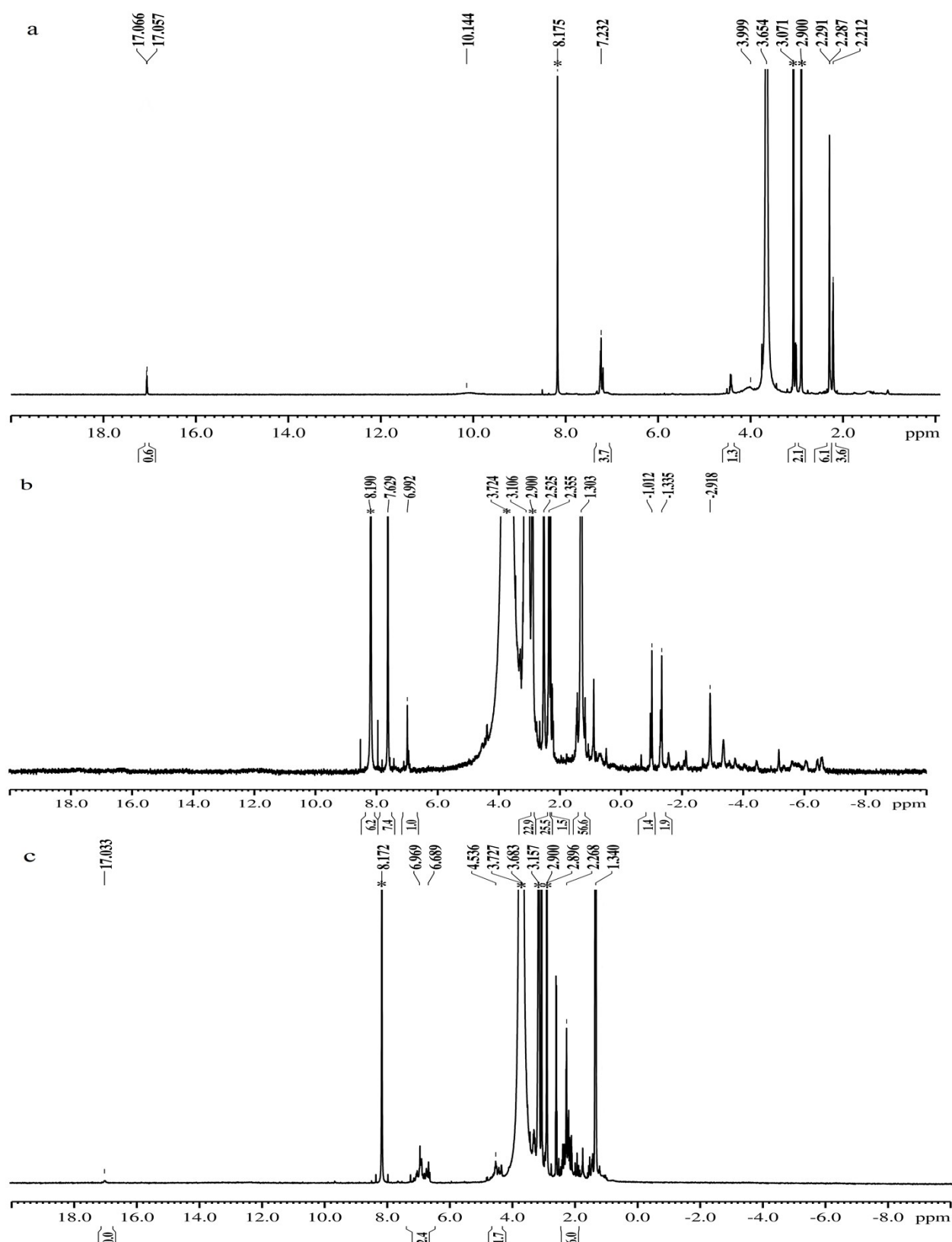


Figure S1. ¹H NMR spectra of **1** (a); **1**:Tb(NO₃)₃:TEA (1:1:8) (b); **1**:Lu(NO₃)₃:TEA (c) (DMF-d₇, 303 K). (C_L = 3 mM) (C_{Ln3+} = 3 mM) and TEA (C_{TEA} = 24 mM). Asterisks in the spectra mark solvent peaks. The doubling signals of solvent are observed in the spectra of **1** with metal salts. This fact was caused by the loading of the sample into thin-walled glass 3 mm NMR tube which was inserted then into the standard 5 mm ampule usually applied for NMR experiments. A capacity between these tubes was filled up with a solvent DMF-d₇.

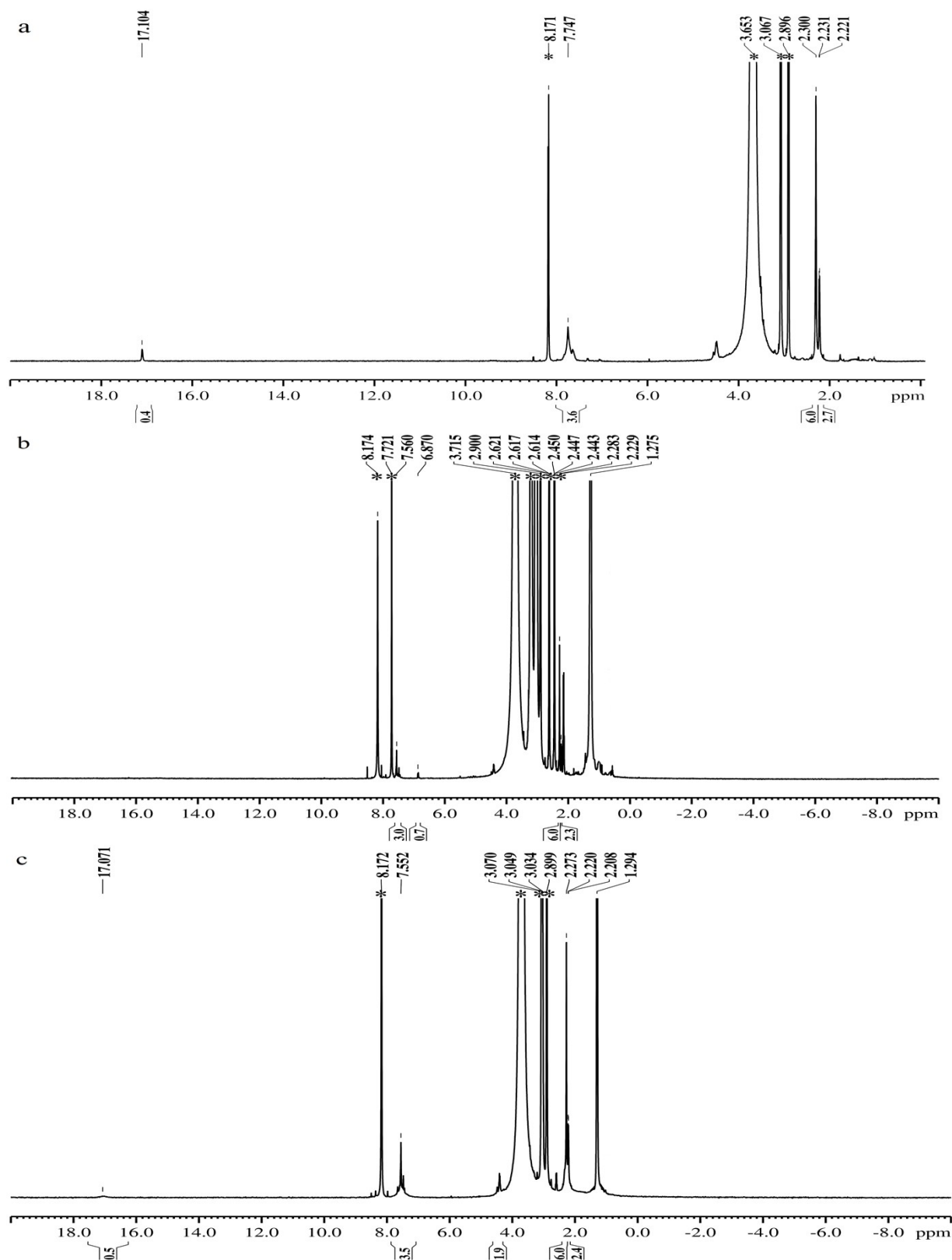


Figure S2. ^1H NMR spectra of **2** (a), **2**: $\text{Tb}(\text{NO}_3)_3$:TEA (1:1:8) (b), **2**: $\text{Lu}(\text{NO}_3)_3$:TEA (c) (DMF-d_7 , 303 K). ($C_{\text{L}} = 3 \text{ mM}$) ($C_{\text{Ln}^{3+}} = 3 \text{ mM}$) and TEA ($C_{\text{TEA}} = 24 \text{ mM}$). Asterisks in the spectra mark solvent peaks. The doubling signals of solvent are observed in the spectra of **2** with metal salts. This fact was caused by the loading of the sample into thin-walled glass 3 mm NMR tube which was inserted then into the standard 5 mm ampule usually applied for NMR experiments. A capacity between these tubes was filled up with a solvent DMF-d_7 .

4. MALDI TOF mass spectra of the L-Tb³⁺-TEA system.

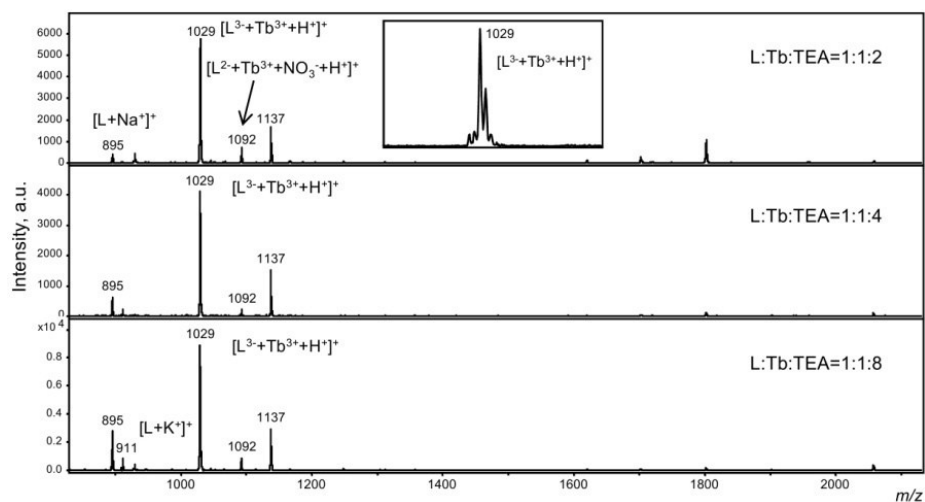


Figure S3. MALDI TOF mass spectra of the L(1)-Tb³⁺-TEA (1:1:2, 1:1:4, 1:1:8) system.

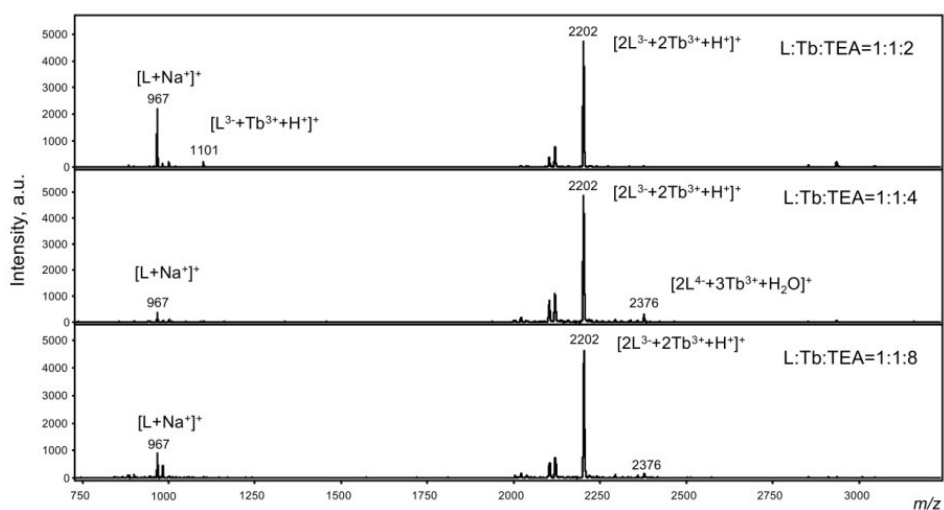


Figure S4. MALDI TOF mass spectra of the L(2)-Tb³⁺-TEA (1:1:2, 1:1:4, 1:1:8) system.

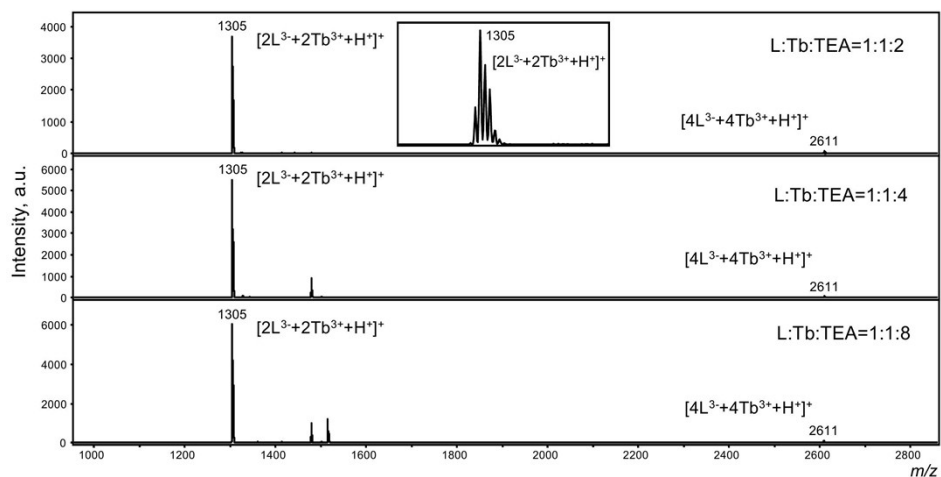


Figure S5. MALDI TOF mass spectra of the L(4)-Tb³⁺-TEA (1:1:2, 1:1:4, 1:1:8) system.

5. Optimized coordinates of atoms for ligands 2,4 and their Tb³⁺ complexes

Cartesian coordinates (in Å) for [Tb(H₂O)₈]³⁺ optimized at the PBE/L1 level

25			
Tb (III)	aquacomplex		
O	2.42993484	-2.21703284	-6.82572897
Tb	0.66058470	-2.75241861	-5.27009374
O	0.21929655	-3.09452181	-2.89766708
O	2.68768323	-3.81510568	-4.44733686
O	1.74105561	-0.93340768	-4.08824431
O	-0.14118400	-3.43251213	-7.46339605
O	-1.74352427	-2.69138764	-4.97150885
O	-0.11909518	-0.67439347	-6.27655035
O	0.17768312	-5.11698241	-5.15332699
H	0.02955297	-5.72033700	-5.91507494
H	0.05877739	-5.67342886	-4.35189907
H	-2.35215152	-3.42489137	-4.73145346
H	-2.31897202	-1.90324064	-5.08917722
H	0.84097094	-3.41893460	-2.20943598
H	-0.62818767	-2.93274016	-2.42731873
H	1.58064010	-0.68147778	-3.15178697
H	2.42787546	-0.30913319	-4.41176426
H	3.46538488	-3.38948733	-4.02311460
H	2.89956932	-4.77451901	-4.47515865
H	-0.59334596	-0.55698102	-7.12901238
H	-0.02117494	0.23060968	-5.90642986
H	2.44246287	-1.51186759	-7.51029754
H	3.30924946	-2.65269321	-6.88283898
H	-1.06047339	-3.65630710	-7.72940444
H	0.39900251	-3.54331656	-8.27706876

Cartesian coordinates (in Å) for tetracalix[4]arene (ligand 4) optimized at the PBE/L1 level

48			
tetracalix[4]arene			
C	2.32118165	-2.71892042	-7.90502214
C	3.67988191	-2.77695576	-8.28671068
C	4.01938837	-2.99056055	-9.62536787
C	3.03244109	-3.13658547	-10.60014027
C	1.69057491	-3.08357919	-10.22679513
C	1.32298549	-2.87723375	-8.89280498
S	4.98057666	-2.70754451	-7.03787643
C	5.27189688	-0.93875234	-6.83471484
C	4.53097637	-0.19918327	-5.88539120
C	4.87727920	1.14867373	-5.64339533
C	5.94133458	1.73057532	-6.33768433
C	6.66498863	1.00156218	-7.28130132
C	6.32841189	-0.32971215	-7.52041560
S	4.03866215	2.08645525	-4.34976886
C	2.59733712	2.76756795	-5.19444119
C	2.63925052	4.07706375	-5.68513891
C	1.50110206	4.67885035	-6.21920626
C	0.30331784	3.96498535	-6.25467276
C	0.23519742	2.65338885	-5.77722385
C	1.38730138	2.03887177	-5.23851923
O	1.28864808	0.76941285	-4.77268447

S	-1.35561979	1.80270615	-5.73407979
C	-1.35115068	0.82922636	-7.25299080
C	-1.99761474	1.32269024	-8.39137197
C	-2.13061585	0.53884177	-9.53621081
C	-1.61843773	-0.75854350	-9.53949642
C	-0.96245726	-1.27390244	-8.41835882
C	-0.82259047	-0.48140576	-7.25750108
O	3.50138798	-0.74029186	-5.18873378
S	-0.41404775	-2.99303839	-8.41901519
O	-0.19136639	-1.01186129	-6.18123716
O	2.02171705	-2.52156856	-6.59749035
H	3.58318978	4.62337847	-5.62504842
H	-0.60642646	4.42055851	-6.65207512
H	6.89461046	-0.92823653	-8.23754610
H	0.89950484	-3.21837449	-10.96782916
H	5.07771272	-3.04594658	-9.88992712
H	-2.41055520	2.33329756	-8.35607131
H	-1.72542277	-1.39865166	-10.41808861
H	6.19677921	2.76997117	-6.11970936
H	7.49466561	1.46549302	-7.81852286
H	1.54385109	5.70317927	-6.59487525
H	-2.64140257	0.93224667	-10.41742241
H	3.30822987	-3.30305160	-11.64342038
H	3.17708043	-1.57173897	-5.64503905
H	0.09522669	-0.28203643	-5.55681622
H	1.07211329	-2.21433731	-6.50517334
H	2.20026343	0.35979428	-4.69621449

Cartesian coordinates (in Å) for ligand **2** optimized at the PBE/L1 level

112

ligand 2

C	1.44349205	-0.65354647	0.39793867
C	0.16483380	-0.73188882	0.99025446
C	0.03338283	-0.68024600	2.37980969
C	1.14451047	-0.56093036	3.22445324
C	2.40837540	-0.47941426	2.62673714
C	2.57068747	-0.52052366	1.23773501
S	-1.31532690	-0.78606127	-0.04048004
C	-1.52257771	-2.54830981	-0.36935853
C	-2.40923324	-3.29411008	0.41550792
C	-2.70431876	-4.62782644	0.12569502
C	-2.09431259	-5.19997504	-0.99820371
C	-1.20137380	-4.48400688	-1.79697154
C	-0.90003902	-3.13883060	-1.48882216
S	-0.54481618	-5.24502509	-3.29686776
C	1.06387572	-5.87686791	-2.78050433
C	1.19123867	-7.22627977	-2.43062572
C	2.43247614	-7.80866197	-2.15287208
C	3.56704513	-6.98797120	-2.23438395
C	3.47010565	-5.63948655	-2.57823652
C	2.21253807	-5.06172638	-2.86082278
S	4.97814045	-4.66524679	-2.76892937
C	5.14169127	-3.85161905	-1.16672713
C	5.96319149	-4.41652099	-0.18708232
C	6.23399782	-3.75886690	1.01815307
C	5.66618088	-2.49583868	1.21264512

C	4.82983737	-1.91198675	0.25728069
C	4.55498450	-2.58574006	-0.95037786
S	4.20505445	-0.23988412	0.52575542
C	7.10055065	-4.42903481	2.07998745
C	7.84013590	-3.50522105	3.01920039
C	7.38239785	-3.25134633	4.31561793
O	8.04673729	-2.46628238	5.13212906
O	3.74807259	-1.99124376	-1.86678558
C	2.52182152	-9.26730810	-1.74997515
C	3.44950421	-10.18110797	-2.60204519
C	4.89646848	-10.21473132	-2.07040339
O	5.25758103	-9.49446297	-1.15785299
O	2.15662075	-3.75189146	-3.20371027
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C	0.71248622	0.93816162	5.23219098
C	2.01300990	1.77841121	5.17686370
O	3.07054766	1.31108552	5.54739399
O	1.54172737	-0.70583110	-0.95466174
C	9.06235392	-2.85971854	2.61776176
O	9.70166337	-2.10123678	3.40728671
C	9.62284250	-3.07570032	1.23094165
C	3.35809641	-9.89622114	-4.12301620
O	4.32506065	-9.62908049	-4.80641057
C	1.96224349	-9.97569083	-4.71195805
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C	0.16293549	0.90998854	6.68220702
O	0.05754356	-0.13011158	7.29595611
C	-0.23543582	2.24560178	7.28019437
C	6.12291695	-3.83961463	4.89386282
C	5.82697028	-11.20786648	-2.72585722
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H	1.87892257	-0.85795205	5.23126801
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H	-2.98046562	-6.10960993	4.00225517
H	0.65986131	2.87703695	7.41141930
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H	1.03453021	3.71853220	5.01934376
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H	5.35852145	-12.20144202	-2.81502923
H	6.76148223	-11.27304244	-2.15398418
H	5.27198545	-3.73422619	4.20458553
H	5.89627622	-3.32791658	5.83872246
H	6.25728584	-4.91452680	5.10082023
H	9.92254999	-4.12848148	1.09471243
H	10.50234484	-2.43192207	1.10103531
H	8.86987612	-2.84757315	0.46023912
H	-5.87121689	-3.59758982	3.44017633
H	8.90076235	-2.15709810	4.54153177
H	3.41451231	-2.67717034	-2.51536931
H	1.22496483	-3.40300810	-3.08189053
H	0.31628859	-1.65609252	-1.80479749
H	2.48021836	-0.93675005	-1.22280730

Cartesian coordinates (in Å) for $[\text{Tb}4(\text{H}_2\text{O})_5]^+ \text{-(I)}$ optimized at the PBE/L1 level

62

Complex structure (I)

C	2.13112566	4.14686671	-7.05367748
C	3.06691300	3.58662347	-6.18835930
C	2.73385419	2.55813049	-5.29658347
C	1.39429206	2.09957606	-5.24173816
C	0.45021900	2.69243556	-6.11981965
C	0.81654866	3.69374119	-7.01988279
S	4.05121195	1.96377485	-4.21335741
C	5.03539189	1.06785460	-5.42434479
C	4.65826530	-0.22441626	-5.84554333
C	5.40191752	-0.85226009	-6.86872298
C	6.54685723	-0.23057196	-7.38881299
C	6.96296879	1.00461104	-6.89976590
C	6.20227255	1.65083560	-5.92482505
S	-1.29291198	2.29188699	-5.89765102
C	-1.46618710	1.01825392	-7.15342327
C	-2.19209911	1.34733925	-8.30187411
C	-2.42585917	0.41002006	-9.30686106
C	-1.89734516	-0.86881017	-9.16775830
C	-1.14811843	-1.19880120	-8.03391210
C	-0.93615070	-0.29410330	-6.95922098
O	0.98489290	1.11789532	-4.38403324
S	5.06860510	-2.52957335	-7.45674598
C	3.56072263	-2.48281255	-8.47283774

C	3.68528066	-2.68288945	-9.85150780
C	2.56931973	-2.93645781	-10.65526808
C	1.29748377	-2.99796728	-10.08834024
C	1.14030328	-2.75406721	-8.72055802
C	2.25763824	-2.46281834	-7.89970686
O	3.57323038	-0.81730723	-5.26859847
S	-0.48905646	-2.86835045	-7.91710835
Tb	0.55603800	-2.60824583	-5.13361339
O	-1.91837996	-2.80908912	-4.88384457
O	2.06092143	-2.20216259	-6.60972961
O	-0.26617899	-0.66464601	-5.85320577
O	1.09478878	-4.89816197	-6.00347389
H	4.09820802	3.94646073	-6.19443487
H	0.05420187	4.12757772	-7.67008339
H	7.11633497	-0.73957775	-8.16934820
H	0.42490237	-3.22552428	-10.70520502
H	4.68387180	-2.66196692	-10.29427231
H	-2.58720575	2.36181359	-8.39198167
H	-2.05855750	-1.62306186	-9.94163339
H	6.49948194	2.63158355	-5.54695002
H	0.27418218	0.58197288	-4.86906464
H	7.87461322	1.46751849	-7.28291708
H	2.42272951	4.94291284	-7.74164614
H	-3.01423587	0.67487190	-10.18726449
H	2.69681769	-3.09620717	-11.72795535
H	1.39487053	-4.76510258	-6.93140528
H	1.57584245	-5.68828816	-5.69082521
H	-2.59507380	-3.50144302	-5.01313629
H	-2.33016134	-1.96388778	-5.15904928
H	3.03101241	-1.33089179	-5.97856315
O	0.16304689	-3.77542339	-2.85719632
O	2.79022588	-2.89460537	-3.94430036
O	0.87498723	-1.21377247	-3.09849898
H	1.03753825	-3.83851585	-2.41071473
H	-0.28331580	-4.62518058	-2.65553063
H	1.16545239	-0.25802248	-3.22728541
H	0.11284788	-1.18664604	-2.48534219
H	3.27640625	-2.03446727	-4.20280262
H	3.41001268	-3.58513990	-4.27287885

Cartesian coordinates (in Å) for $[\text{Tb}_2\text{4}_2(\text{H}_2\text{O})_4]^{2+}$ -(II) optimized at the PBE/L1 level

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Complex structure (II)

C	0.27720509	0.10256164	0.01274774
C	0.18094696	0.32675345	1.38904474
C	2.57017313	0.23007172	1.60792475
C	2.68334686	0.00289316	0.23189202
C	1.54153314	-0.07563418	-0.61639908
S	-1.22635673	0.10914395	-0.97838705
C	-1.34232307	-3.84117310	-2.02966878
C	-2.28489599	-4.36252163	-1.13590734
C	-2.87103811	-3.54150409	-0.17564621
C	-1.58838518	-1.65353853	-1.01361054
C	-0.98664488	-2.48067934	-1.98126634
S	-0.71899712	-4.91338891	-3.33818382
C	3.25830176	-5.64410558	-2.68644242

C	3.20276412	-6.88878974	-2.05297702
C	1.98338291	-7.50166190	-1.76468447
C	0.80309932	-6.86235600	-2.13302751
C	0.84174244	-5.61510407	-2.76610761
C	2.06982496	-4.95615678	-3.06121432
S	4.86713289	-4.94196085	-3.08872318
C	4.86624613	-1.77112153	-0.50648305
C	5.66010961	-2.24051503	0.54633629
C	6.17571646	-3.53391642	0.51439330
C	5.12250759	-3.89536889	-1.64693139
C	4.59221791	-2.59140957	-1.61621306
S	4.34093246	-0.04672954	-0.47925661
C	5.90761058	-4.35170144	-0.58269357
C	-2.52276881	-2.19236314	-0.12260969
C	1.31767143	0.38391443	2.19537251
O	2.11044178	-3.76807539	-3.67569171
O	1.64707032	-0.28281730	-1.93434863
O	-0.08383731	-1.98098541	-2.88522851
O	3.83773613	-2.10359489	-2.65311850
Tb	3.44268341	0.24853635	-3.20484584
Tb	0.51437172	-2.94827252	-5.05272454
C	2.73017145	3.04632001	-5.45139503
C	2.66576126	4.31425732	-6.04069849
C	0.27955194	4.08950137	-6.26108663
C	0.32532988	2.82393748	-5.66649368
C	1.56081385	2.28904807	-5.25402075
S	4.31739100	2.47980989	-4.81091463
C	5.60798965	-0.69493845	-7.05429625
C	6.48750040	-0.06103489	-7.93646812
C	6.66847044	1.32179615	-7.91088565
C	5.08240758	1.45741636	-6.08571400
C	4.86423466	0.04964757	-6.09585863
S	5.47347395	-2.49026550	-7.09746188
C	1.65728151	-2.83080986	-8.52666144
C	1.86747558	-3.10567762	-9.88285274
C	3.16081230	-3.15338669	-10.39738649
C	4.24507003	-2.94087810	-9.54680191
C	4.05278071	-2.67270693	-8.18726898
C	2.74713206	-2.61548232	-7.66333436
S	-0.02580723	-2.91831206	-7.88662465
C	-1.23140162	0.83869885	-6.78614720
C	-1.96228066	1.22729077	-7.91238219
C	-2.06266889	0.40124847	-9.03187016
C	-0.69604869	-1.24300513	-7.89413786
C	-0.56203218	-0.41674043	-6.74131834
S	-1.20107353	1.92445482	-5.34973183
C	-1.43328969	-0.84010996	-9.01316625
C	5.96808322	2.07679833	-6.97445479
C	1.44195274	4.83511791	-6.45391836
O	2.52306064	-2.37765248	-6.33084278
O	1.63965929	1.06147243	-4.64681683
O	4.02557546	-0.54681853	-5.24050229
O	0.13409142	-0.80334099	-5.66580352
H	-0.81100094	0.46778603	1.82433665
H	3.47775503	0.29506985	2.21287701
H	-2.55736207	-5.41818881	-1.20521221
H	4.14227029	-7.38239970	-1.79411977
H	-0.16467724	-7.33185371	-1.94097855

H	5.87343465	-1.57823915	1.38855861
H	6.31927573	-5.36196321	-0.63448886
H	-2.98616696	-1.52893720	0.61082318
H	0.45020160	-1.18396944	-2.48435965
H	3.31141943	-2.86425633	-3.12633152
H	3.58553787	4.89005746	-6.16694581
H	-0.69143958	4.48951578	-6.56100144
H	7.04384115	-0.67641790	-8.64718539
H	1.00556705	-3.28701625	-10.52914917
H	5.26712435	-2.99359095	-9.92812272
H	-2.46706955	2.19591396	-7.89536877
H	-1.51643264	-1.51653837	-9.86723495
H	6.10994499	3.15867855	-6.91688900
H	3.26946365	-1.78004570	-5.92412304
H	0.88873886	0.42523078	-4.98229758
H	1.22816561	0.56081660	3.26861064
H	6.79298671	-3.89989068	1.33699534
H	1.95452320	-8.47439997	-1.27063046
H	-3.60437771	-3.94942078	0.52253199
H	7.35937178	1.80377648	-8.60478261
H	1.39291768	5.82312836	-6.91551480
H	-2.63766922	0.71669462	-9.90423108
H	3.32370387	-3.36567846	-11.45570231
O	2.92630760	2.34378790	-2.01697769
O	5.90585502	0.27762833	-3.16141558
H	3.28849175	3.24982663	-2.05869271
H	2.29363887	2.32155922	-1.26830557
H	6.56159454	0.53102270	-2.48338000
H	6.39639003	0.14818804	-4.00041757
O	1.01126373	-5.17171910	-5.99037429
O	-1.92914581	-2.85005708	-5.34774900
H	0.67754061	-5.66250515	-6.76605692
H	1.54523839	-5.80091609	-5.46095881
H	-2.65192067	-3.49002301	-5.19980186
H	-2.32181509	-2.07243306	-5.79777659

Cartesian coordinates (in Å) for $[\text{Tb}_2\text{4}_2(\text{H}_2\text{O})_4]^{2+}$ -(III) optimized at the PBE/L1 level

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Complex structure (III)

C	1.68087105	4.80214124	-6.58144709
C	2.86543632	4.21767201	-6.14148375
C	2.84477650	2.97065114	-5.50547474
C	1.62760508	2.29859466	-5.29054235
C	0.43151938	2.90041827	-5.72627896
C	0.47085806	4.14382154	-6.36544628
S	4.39174406	2.35010024	-4.81979534
C	5.14587220	1.29035364	-6.07344016
C	4.82489378	-0.08223978	-6.16055431
C	5.52928631	-0.88667689	-7.08131206
C	6.51087197	-0.31263925	-7.89703860
C	6.81708412	1.04546101	-7.81088222
C	6.14047434	1.84270380	-6.89156004
S	-1.14984770	2.10864039	-5.38989871
C	-1.24535857	1.00959890	-6.81320583
C	-1.92342853	1.43935356	-7.95743314
C	-2.05230074	0.61362394	-9.07354035

C	-1.50455232	-0.66582334	-9.03336343
C	-0.82180152	-1.10798105	-7.89579938
C	-0.66869867	-0.28800594	-6.74406014
O	1.61689340	1.08614858	-4.64355041
Tb	3.34540348	0.23812402	-3.10119571
O	5.82469573	0.20077620	-3.06063957
S	5.27061981	-2.66762618	-7.12431640
C	3.81578690	-2.79344619	-8.17616280
C	3.98855245	-3.11583119	-9.52571177
C	2.89493202	-3.31327970	-10.36879860
C	1.60927149	-3.19185663	-9.84869901
C	1.42003508	-2.86185632	-8.50171751
C	2.51593912	-2.65280837	-7.61952353
O	3.87161188	-0.61165334	-5.33496215
S	-0.26801918	-2.82530113	-7.86285683
Tb	0.46417628	-2.82865677	-5.11211821
O	-2.01435430	-2.82402161	-5.19308916
O	2.32899959	-2.35498307	-6.32652908
O	-0.03321050	-0.71474526	-5.64346554
S	4.19526017	0.14729650	-0.38607049
C	4.83281892	-1.54039867	-0.45016644
C	5.66791359	-1.97053554	0.58746046
C	6.25039405	-3.23422736	0.54309244
C	6.00124113	-4.05717901	-0.55529871
C	5.17557136	-3.63877243	-1.60327720
C	4.55912360	-2.35865391	-1.58086525
S	4.99316694	-4.70745623	-3.03973258
C	3.42477029	-5.51758891	-2.68711104
C	3.42143400	-6.81687082	-2.16721272
C	2.22960547	-7.51846239	-1.98572757
C	1.02250713	-6.91922572	-2.33555120
C	1.00251653	-5.61469396	-2.84686784
C	2.20456811	-4.89525718	-3.02607067
S	-0.58190446	-4.94079638	-3.39354666
C	-1.22845566	-3.93522462	-2.04478928
C	-2.11625307	-4.53937265	-1.14656353
C	-2.74149311	-3.78220462	-0.15957804
C	-2.49120045	-2.41251032	-0.08566840
C	-1.61193593	-1.79181701	-0.97884894
C	-0.96688439	-2.55482146	-1.97101962
S	-1.36674571	-0.00964403	-0.91156298
C	0.12970377	0.05103498	0.08831640
C	0.01447662	0.20963236	1.47226362
C	1.14347611	0.29406069	2.28611733
C	2.40461873	0.23239036	1.69930572
C	2.53452811	0.07182068	0.31617914
C	1.40290460	-0.02288477	-0.53983136
O	1.52223659	-0.15594280	-1.86851187
O	-0.11218740	-1.96810042	-2.87322546
O	2.17012991	-3.63360874	-3.55305502
O	3.77314336	-1.93487427	-2.57993570
O	2.82818804	2.45378277	-2.11485145
O	1.02577970	-5.04533583	-6.07168270
H	-0.98525684	0.27561561	1.90752175
H	3.30506241	0.31953901	2.31222833
H	-2.31826752	-5.60907844	-1.23670752
H	4.37931916	-7.27976871	-1.91986820
H	0.07969379	-7.45882634	-2.21999796

H	5.86031260	-1.30002005	1.42858090
H	6.46259907	-5.04527938	-0.61945306
H	-2.99014309	-1.79764738	0.66647592
H	0.33996001	-1.13596715	-2.45959929
H	3.82094896	4.72883949	-6.27899436
H	-0.47097570	4.59700614	-6.68213977
H	7.04757056	-0.95772016	-8.59619741
H	0.73571426	-3.35776578	-10.48388627
H	5.00597513	-3.22408217	-9.90838866
H	-2.36208030	2.43978077	-7.95802652
H	-1.61190836	-1.34079324	-9.88598234
H	6.37913972	2.90430357	-6.79428168
H	0.81120166	0.51624202	-4.95006604
H	1.04124162	0.42041483	3.36532607
H	6.89979153	-3.57243888	1.35246479
H	2.24292187	-8.53315141	-1.58328769
H	-3.43266953	-4.25536438	0.54036693
H	7.58846632	1.47839857	-8.45061973
H	1.69926222	5.77409793	-7.07792388
H	-2.58618137	0.95903941	-9.96053981
H	3.04455337	-3.56794163	-11.41948813
H	3.42534710	3.18071770	-1.84920563
H	2.05475489	2.49770460	-1.51550051
H	6.23890638	-0.48814112	-2.49782512
H	6.34239123	0.21954694	-3.89263789
H	1.53151702	-5.03832481	-6.91258905
H	1.42867025	-5.74651403	-5.51795954
H	-2.63797775	-3.53119515	-5.45116882
H	-2.44414885	-1.97611434	-5.42905711
H	2.96426474	-3.02258173	-3.19446524
H	3.36109947	-1.43292170	-5.77941762

Cartesian coordinates (in Å) for [Tb₂2₂(H₂O)₄]-**(IV)** optimized at the PBE/L1 level

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Complex structure (IV)

C	0.261993900	-0.516148610	0.128125520
C	0.173296600	-0.902823900	1.463360950
C	2.539931480	-0.602173120	1.725754000
C	2.657258190	-0.224872550	0.381898180
C	1.510398440	-0.169358540	-0.422329150
S	-1.177606160	-0.451775750	-0.957864930
C	-1.450736620	-4.436610430	-1.853577860
C	-2.337806270	-4.885653660	-0.875439190
C	-2.900764890	-4.008859200	0.059123930
C	-1.631550030	-2.194247440	-0.984115950
C	-1.071465540	-3.060638330	-1.974115680
S	-0.743587220	-5.613599670	-3.019096070
C	3.284461830	-5.491133940	-2.311569670
C	3.388465670	-6.247897610	-1.146332210
C	2.272418070	-6.845022680	-0.545209930
C	1.030172170	-6.654508870	-1.157307000
C	0.903476730	-5.891147240	-2.319914060
C	2.031675630	-5.307878040	-2.964404340
S	4.732967420	-4.676211870	-3.023376510
C	4.981117350	-1.518086190	-0.437248520
C	5.804671380	-2.026462300	0.574178160

C	6.319083020	-3.319816160	0.501193540
C	5.161477560	-3.601836830	-1.646554720
C	4.598862290	-2.284334050	-1.585967610
S	4.302415470	0.146488110	-0.276861400
C	5.996868740	-4.074974200	-0.635869530
C	-2.527068420	-2.663058770	-0.019928270
C	1.307930700	-0.954355070	2.284867580
C	2.369455610	-7.639688750	0.739286280
C	1.177912980	-1.369714030	3.731487390
C	-3.887960040	-4.471967250	1.125228150
C	7.156190220	-3.929056330	1.620255880
C	7.012312800	-3.267545950	2.973712610
C	3.398317630	-8.806387850	0.775585280
C	0.403640290	-0.341327910	4.605538350
O	1.924070510	-4.645802790	-4.099742380
O	1.593878360	0.227365530	-1.739753750
O	-0.288036610	-2.636489930	-2.922938660
O	3.810036950	-1.798166110	-2.505199340
C	-3.709972340	-5.893492140	1.607343780
C	5.870433760	-3.463589270	3.765633340
C	8.015389440	-2.375752840	3.479775240
C	4.764371540	-8.375438310	1.351126100
C	3.506360330	-9.600692760	-0.550765060
C	1.143715650	-0.147412960	5.948149720
C	-1.066860180	-0.755251370	4.819916980
C	-2.637645710	-6.244113770	2.486976990
C	-4.573631240	-6.931981760	1.222444980
O	-2.494200030	-7.447384140	2.903169400
O	-4.403300630	-8.145528620	1.664121840
C	-1.634420010	-5.221690190	2.951054590
C	-5.745456840	-6.737447080	0.293484870
O	0.775178810	-0.683123550	6.973674980
O	-1.523615000	-1.783323450	4.356663740
C	-1.908469670	0.204503510	5.630522940
C	2.369831710	0.743374190	5.886453580
O	5.006832890	-7.207358330	1.604767120
O	4.559332720	-9.809223350	-1.117999310
C	2.189438780	-10.122371670	-1.091089200
C	5.765890270	-9.476043720	1.603658910
O	5.744849040	-2.860829160	4.928002190
C	4.684491670	-4.277083060	3.340336660
O	7.891148530	-1.806193170	4.609485470
C	9.266516310	-2.064732620	2.685950990
Tb	3.772257980	0.278928120	-3.254670780
Tb	0.325278620	-3.294885930	-4.937468800
C	3.141426930	3.015550490	-5.447679180
C	2.993462960	4.256548470	-6.069314160
C	0.624828510	3.928442070	-6.124406850
C	0.743729750	2.677784000	-5.512600130
C	2.028278590	2.157380900	-5.157001810
S	4.811133110	2.473127010	-4.996162540
C	5.453008960	-0.777403180	-7.370415890
C	5.916446870	-0.182589570	-8.542856570
C	6.069244030	1.202207770	-8.667455380
C	5.271299640	1.408715840	-6.378823370
C	5.148635740	-0.002546860	-6.213041850
S	5.213612380	-2.571309200	-7.321498770
C	1.363700620	-2.929322480	-8.598867580

C	1.494709520	-2.884239300	-9.989246700
C	2.743312790	-2.751378960	-10.609974580
C	3.871923750	-2.686588370	-9.784302210
C	3.768430610	-2.713430960	-8.390741380
C	2.504602660	-2.841971910	-7.783179960
S	-0.297605650	-3.052707730	-7.896339840
C	-0.940347940	0.752324520	-6.609951470
C	-1.432669840	1.353696040	-7.768402880
C	-1.617347840	0.653497120	-8.968516340
C	-0.778199480	-1.319969080	-7.832365510
C	-0.608624410	-0.637932410	-6.590032610
S	-0.746775410	1.746963800	-5.115411550
C	-1.282222480	-0.702436490	-8.976456740
C	5.735461290	1.987373660	-7.560024540
C	1.727915990	4.740137210	-6.425395250
C	2.881868470	-2.612750000	-12.113070800
C	1.543033740	6.060482660	-7.146746360
C	6.576738980	1.819898270	-9.964553020
C	-2.171797810	1.341151410	-10.209300900
C	-1.440309730	2.611707000	-10.596890710
C	2.242099560	-3.723379130	-12.994584300
C	2.041501200	7.341007390	-6.414194780
O	2.392510320	-2.891814420	-6.418576940
O	2.183300140	0.997336670	-4.576627770
O	4.793177390	-0.547971550	-5.075171900
O	-0.189645790	-1.255805170	-5.518768280
C	5.863811510	1.314288530	-11.201837620
C	-0.148623210	2.528334100	-11.241194150
C	-1.932123980	3.888963730	-10.323911410
C	0.770179670	-3.437060400	-13.348688340
C	2.467285640	-5.148098720	-12.429435490
C	3.521654240	7.655053240	-6.707419780
C	1.700230000	7.332432520	-4.906271160
C	4.528898490	1.744182080	-11.503243090
C	6.447859680	0.392490400	-12.079759930
O	3.898899180	1.265004460	-12.507664410
O	5.790590470	-0.069380940	-13.115865900
C	3.832983030	2.772430960	-10.652908280
C	7.855722860	-0.129771800	-11.935108830
O	4.219632600	6.904047060	-7.363191530
O	2.541944920	7.412878630	-4.033745030
C	0.224010520	7.205511020	-4.577540460
C	4.047181880	8.964052610	-6.163126640
O	0.155150520	-2.517116950	-12.840718700
O	1.561119680	-5.924863560	-12.205010510
C	3.915283220	-5.516303540	-12.168507960
C	0.144052760	-4.347998900	-14.378523640
O	0.516678640	3.572004440	-11.521859960
C	0.443580320	1.188781730	-11.599520910
O	-1.239224760	4.971488430	-10.622116320
C	-3.253477530	4.195299270	-9.673917270
H	-0.800022590	-1.188711260	1.869876430
H	3.447826860	-0.635867990	2.335013020
H	-2.577689030	-5.952344070	-0.829092630
H	4.367161720	-6.356857360	-0.675892800
H	0.129968020	-7.093084920	-0.713889730
H	6.026173420	-1.402715270	1.444926010
H	6.392715890	-5.090326540	-0.733025210

H	-2.940412240	-1.946439670	0.697039520
H	1.372554690	-8.036858290	0.988437320
H	2.669636850	-6.953207620	1.549909310
H	2.176474790	-1.565064430	4.154741790
H	0.602182780	-2.309182430	3.793249190
H	-4.915976280	-4.349609610	0.740441400
H	-3.817083400	-3.775161100	1.979376260
H	8.220439050	-3.923297930	1.326028680
H	6.879161310	-4.996582470	1.694801600
H	3.013965190	-9.552150680	1.501953410
H	0.386622620	0.636549040	4.088557080
H	-1.169714640	-4.715309730	2.090109790
H	-0.865462040	-5.724300470	3.552134290
H	-2.113492080	-4.438055180	3.560729760
H	-6.150463040	-7.723112970	0.027561630
H	-5.452940060	-6.199699000	-0.621259100
H	-6.539314820	-6.151915320	0.786362790
H	-1.598011250	0.118054560	6.684628920
H	-2.970197790	-0.058619630	5.538291760
H	-1.739513010	1.247610340	5.318583180
H	2.035069780	1.791412310	5.790087580
H	2.993541920	0.526882750	5.005755620
H	2.956210040	0.635786000	6.808238430
H	1.580668170	-10.577982830	-0.293921410
H	2.389282820	-10.850113390	-1.888673960
H	1.613255840	-9.278953950	-1.507513430
H	6.082004590	-9.867171860	0.622342150
H	5.307119380	-10.314063200	2.153240680
H	6.625909290	-9.078244820	2.157601260
H	3.975670720	-3.612853270	2.814153530
H	4.176184380	-4.669111980	4.233882420
H	4.925957490	-5.088403410	2.644745710
H	9.911668650	-2.955889410	2.609210330
H	9.817601840	-1.269697660	3.205781910
H	9.025485580	-1.741098690	1.661170610
H	3.879987890	4.853676940	-6.295126280
H	-0.382435030	4.271408170	-6.383223060
H	6.147127180	-0.822918420	-9.397607350
H	0.593003120	-2.922989860	-10.602872440
H	4.865498710	-2.592803020	-10.230755820
H	-1.672912220	2.419451600	-7.727671370
H	-1.405943540	-1.290847370	-9.891275820
H	5.826051350	3.077049520	-7.614559710
H	3.951170270	-2.528923400	-12.360665710
H	2.409860020	-1.661724850	-12.415987890
H	0.476021140	6.180044980	-7.390983720
H	2.093761420	6.028193630	-8.102192700
H	7.658621090	1.627708530	-10.059546630
H	6.480208850	2.916478600	-9.886737950
H	-3.239912530	1.562675690	-10.048279140
H	-2.144639490	0.619960410	-11.043934100
H	2.784208580	-3.718320440	-13.962136420
H	1.473937050	8.199079060	-6.829716200
H	3.642877840	2.363580430	-9.646004790
H	2.880854660	3.065607190	-11.115809690
H	4.468848280	3.662137860	-10.517604290
H	8.034378040	-0.880665020	-12.716375580
H	8.026433500	-0.583150240	-10.946719070

H	8.587810410	0.685621460	-12.053505790
H	0.063563850	7.476213590	-3.525308730
H	-0.084597390	6.156845970	-4.725413210
H	-0.396089610	7.831021990	-5.238527310
H	5.045211880	9.161796290	-6.574971090
H	4.097967680	8.872157190	-5.065757590
H	3.363704920	9.797957450	-6.391504380
H	4.568247980	-5.200851920	-12.997518180
H	3.988429980	-6.600336320	-12.009239790
H	4.261704050	-4.998786730	-11.258379660
H	0.043617370	-5.346728410	-13.922377080
H	0.789645760	-4.454933060	-15.265318650
H	-0.841409910	-3.959930460	-14.666231360
H	0.598892410	0.587367030	-10.688748410
H	1.402795720	1.335335920	-12.113697630
H	-0.238513300	0.612175740	-12.245224640
H	-3.961962490	3.360131900	-9.723662780
H	-3.689568380	5.078589340	-10.163929950
H	-3.098244510	4.451466980	-8.612061190
H	-0.341473790	4.577598590	-11.060486620
H	4.797776860	0.456743150	-13.020724290
H	-3.473852310	-8.043521790	2.329055820
H	6.676070130	-2.296899240	5.013374760
O	6.239615060	0.036977430	-2.906804220
O	3.114469270	2.517771970	-2.236397820
O	-2.109801840	-3.640343420	-5.247128520
O	0.565404010	-5.544778920	-6.104074780
H	-2.558070880	-2.915700250	-4.765226040
H	-2.371587090	-4.464280360	-4.786949880
H	1.333204170	-5.589794780	-5.461608220
H	0.938544710	-5.626403550	-7.001018040
H	6.228895020	-0.437999860	-3.777821050
H	6.418957480	-0.654107300	-2.231509400
H	2.233354500	2.197679570	-1.939853480
H	2.918101350	3.155632780	-2.957923170
H	3.323367040	-2.798447280	-6.053618030
H	0.721588180	-0.031562010	-2.166114480

Cartesian coordinates (in Å) for [Tb₂2₂(H₂O)₄](V) optimized at the PBE/L1 level

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Complex structure (V)

C	1.216001930	-0.577755990	0.127322870
C	1.230404680	-1.102869260	1.417948570
C	3.564133520	-1.624906170	1.176943960
C	3.577132610	-1.094021930	-0.118325570
C	2.383930650	-0.590916910	-0.660267280
S	-0.247151220	0.183961520	-0.594607010
C	-1.660288340	-3.322344540	-2.186444300
C	-2.903899700	-3.403225350	-1.556551310
C	-3.355594460	-2.418518060	-0.670128400
C	-1.238732110	-1.256696600	-1.014856180
C	-0.780059250	-2.209927390	-1.977176290
S	-1.249983340	-4.583983650	-3.386643360
C	2.584939040	-5.875517010	-2.851707520
C	2.492731620	-6.675745380	-1.715696030
C	1.278909300	-6.791598180	-1.023219510

C	0.161984820	-6.118891910	-1.536458060
C	0.232264110	-5.310277600	-2.676911830
C	1.468510670	-5.156805220	-3.321720500
S	4.109869350	-5.707346010	-3.795128280
C	5.482502410	-2.626949180	-1.466392460
C	6.637970310	-3.203845510	-0.932229440
C	7.052425370	-4.493356540	-1.281489760
C	5.070487040	-4.658757110	-2.696561480
C	4.654902080	-3.322317750	-2.406117960
S	5.118429420	-0.929383810	-1.030234610
C	6.232957740	-5.212097210	-2.155869550
C	-2.488688390	-1.357847540	-0.397577800
C	2.400753610	-1.653934840	1.957483340
C	1.156124790	-7.600541160	0.253282020
C	2.411248810	-2.193327220	3.369455890
C	-4.708510190	-2.562868470	0.018779270
C	8.333140420	-5.114832460	-0.738550950
C	8.703635200	-4.745658910	0.681249900
C	1.652611270	-9.074217690	0.219471370
C	2.595735470	-1.086234960	4.426997510
O	1.597789230	-4.320561160	-4.391239470
O	2.347806760	-0.111650470	-1.937198790
O	0.347866900	-2.077092800	-2.618684660
O	3.594503340	-2.784205350	-2.947734910
C	-5.370729460	-1.275744040	0.455147410
C	8.035385880	-5.329117840	1.767602880
C	9.740362020	-3.804780250	0.984361340
C	3.139584480	-9.213349530	0.601512070
C	1.273281060	-9.826505300	-1.082051950
C	4.069591360	-0.615273440	4.462066900
C	2.144788540	-1.564604920	5.827604860
C	-6.038859200	-0.425387620	-0.493805250
C	-5.363266090	-0.856988200	1.787426270
O	-6.611869490	0.649273010	-0.136721320
O	-5.956505490	0.257003170	2.159193490
C	-6.074312660	-0.797738570	-1.957608400
C	-4.697797070	-1.616994090	2.904025080
O	4.972417250	-1.414232330	4.604987310
O	1.661855710	-2.662618140	6.005698500
C	2.325420660	-0.569203840	6.959356240
C	4.308733380	0.866473570	4.265358120
O	3.852837060	-8.240284290	0.762628630
O	2.074758790	-10.445663180	-1.752474250
C	-0.192432450	-9.750790380	-1.464504240
C	3.651037030	-10.623041890	0.792617440
O	8.357071100	-5.032004760	3.003494630
C	6.920408160	-6.320398640	1.607713430
O	10.050559010	-3.518745450	2.184444470
C	10.516315390	-3.108887130	-0.116632080
C	1.538950040	2.644560720	-4.537280270
C	1.057591590	3.935393790	-4.770182120
C	-1.025419430	3.048147280	-5.517842210
C	-0.565224930	1.746310340	-5.305429880
C	0.747655390	1.471565880	-4.793826700
S	3.165256950	2.480950670	-3.794031870
C	5.272323500	0.179036130	-6.455198130
C	5.592592800	1.103727520	-7.449525640
C	5.184546150	2.441250310	-7.351121270

C	4.099127140	1.904164550	-5.216847830
C	4.523892020	0.570253380	-5.323763490
S	5.885405800	-1.515130010	-6.477275120
C	2.599937550	-3.426569320	-8.040111470
C	3.125031030	-3.875587500	-9.254542470
C	4.443279260	-3.602991930	-9.642107400
C	5.215945800	-2.841936950	-8.758244150
C	4.712486880	-2.369389770	-7.543849920
C	3.370682360	-2.642735310	-7.113177650
S	0.938932570	-3.949253750	-7.602298670
C	-1.108102640	-0.445134450	-7.008511030
C	-1.362235060	-0.031323580	-8.316238400
C	-0.925020340	-0.788936690	-9.411669820
C	0.053709380	-2.404209140	-7.844431780
C	-0.398602670	-1.639773270	-6.757029160
S	-1.762198500	0.428063670	-5.574390290
C	-0.238941520	-1.978227640	-9.142632810
C	4.457810140	2.813499110	-6.215090860
C	-0.234181060	4.172210830	-5.257581140
C	5.034886550	-4.049341050	-10.965228130
C	-0.776014290	5.558241460	-5.548849770
C	5.571264950	3.479093160	-8.397825980
C	-1.239101640	-0.382496340	-10.846401690
C	-0.294025800	0.650051770	-11.459696060
C	4.589611470	-5.430795410	-11.507609530
C	-0.355954570	6.696083230	-4.584373150
O	2.897988670	-2.223777480	-5.979561240
O	1.177489160	0.266908220	-4.573664260
O	4.254939300	-0.326502120	-4.342210350
O	-0.193753530	-2.052391430	-5.481374350
C	4.677874660	3.529615090	-9.636725400
C	0.955115190	0.228983900	-11.990333050
C	-0.697656880	2.007574680	-11.546647440
C	3.339206770	-5.330072400	-12.405183000
C	4.536910450	-6.541581760	-10.420249900
C	0.939492520	7.398755670	-5.039928960
C	-0.397600340	6.288727340	-3.084097220
C	3.444276240	4.232939110	-9.583429170
C	5.115876000	2.925218490	-10.843557660
O	2.592654900	4.261974360	-10.556702950
O	4.404566920	2.837090230	-11.916366010
C	3.025506620	5.022588540	-8.371561580
C	6.510129140	2.340016910	-10.968589460
O	1.536844190	7.039535080	-6.039881390
O	0.491065610	6.536473540	-2.294601560
C	-1.662102880	5.570516390	-2.656111380
C	1.397832090	8.575001470	-4.213108050
O	2.787074420	-4.261800870	-12.604341680
O	3.614195600	-7.321423740	-10.299408860
C	5.754680650	-6.607193060	-9.519749990
C	2.867809490	-6.608091830	-13.054577360
O	1.846217890	1.041884640	-12.457617480
C	1.344986780	-1.223662050	-12.061042620
O	0.055880620	2.968549090	-11.963097740
C	-2.101875210	2.436263510	-11.163650920
Tb	2.248038450	3.269798690	-12.565176990
H	0.306145840	-1.087260430	2.003291990
H	4.501873380	-2.013001930	1.585112240

H	-3.533404490	-4.273102130	-1.772552140
H	3.383968100	-7.188572010	-1.349801720
H	-0.809131440	-6.217523780	-1.041166440
H	7.212305500	-2.625645380	-0.202726660
H	6.486838840	-6.244293250	-2.417793480
H	-2.787861640	-0.577288180	0.307978180
H	0.102789250	-7.585156670	0.573780800
H	1.745465390	-7.101942770	1.042280980
H	3.230713110	-2.917309880	3.502022850
H	1.471238220	-2.721199400	3.594713870
H	-4.593509210	-3.221610010	0.897475930
H	-5.380908160	-3.113617760	-0.663004210
H	9.168854940	-4.844102070	-1.407023120
H	8.238840130	-6.212130750	-0.826667700
H	1.100170430	-9.620254020	1.012539090
H	1.958577190	-0.215433740	4.180775010
H	-5.056170290	-0.968414830	-2.342175390
H	-6.562344100	0.010598850	-2.517468890
H	-6.638131030	-1.734238530	-2.105182380
H	-4.660701350	-0.975692240	3.794935470
H	-3.679036340	-1.927573530	2.629055310
H	-5.271085390	-2.526158200	3.151035000
H	3.401087530	-0.387624650	7.123632800
H	1.880763920	-0.972031280	7.878857090
H	1.862779440	0.398992640	6.707775700
H	3.684030740	1.466612890	4.946805000
H	4.005932490	1.130231150	3.236361170
H	5.371735810	1.102203720	4.407696230
H	-0.846015960	-9.894713440	-0.589480510
H	-0.402436870	-10.505770710	-2.233669790
H	-0.404405590	-8.749938350	-1.876568940
H	3.656655730	-11.109428120	-0.196702660
H	2.978845420	-11.208721430	1.440719930
H	4.663446740	-10.595219850	1.215824240
H	6.105231280	-5.901819730	0.997614500
H	6.536021030	-6.599107280	2.597147660
H	7.273185570	-7.227040400	1.088965210
H	11.129666740	-3.832130510	-0.679466460
H	11.177182330	-2.363580080	0.345460500
H	9.843701320	-2.614811330	-0.835181950
H	1.731350280	4.767482270	-4.552996630
H	-2.045137610	3.177313170	-5.895963270
H	6.198130530	0.762785060	-8.293295850
H	2.465829430	-4.458340530	-9.902174340
H	6.254917750	-2.604600990	-9.010740500
H	-1.939075110	0.885501280	-8.462892100
H	0.070164440	-2.631786990	-9.961449590
H	4.168867580	3.856051040	-6.064631310
H	6.133070710	-4.030286990	-10.878256790
H	4.758150860	-3.321788380	-11.749631070
H	-1.875687570	5.500733100	-5.585408160
H	-0.433177890	5.878892680	-6.549217570
H	6.610167060	3.290755040	-8.704068800
H	5.585911690	4.467211410	-7.910008930
H	-2.269238500	0.000086400	-10.879818210
H	-1.246317760	-1.293825990	-11.466065670
H	5.389314000	-5.788158820	-12.191312380
H	-1.133780990	7.486785000	-4.651018730

H	2.511575040	4.356041560	-7.656562600
H	2.306816120	5.798658480	-8.668089590
H	3.861936660	5.491181660	-7.836938870
H	6.713326140	2.141629250	-12.030288420
H	6.577994150	1.385518580	-10.421160650
H	7.290396260	3.005968950	-10.570786150
H	-1.694490680	5.523300680	-1.559873780
H	-1.650094170	4.545652160	-3.063317850
H	-2.560943880	6.072526460	-3.048872010
H	2.243098850	9.071287910	-4.707228490
H	1.684214270	8.192605490	-3.219425200
H	0.573285770	9.288841250	-4.050646470
H	6.687472850	-6.547613460	-10.103474200
H	5.721228080	-7.538280880	-8.939228180
H	5.739903170	-5.747452820	-8.829160070
H	2.520388120	-7.280937780	-12.253162940
H	3.700442090	-7.124207360	-13.560768290
H	2.062399690	-6.389124720	-13.767533060
H	1.807093070	-1.528531990	-11.105428650
H	2.098968550	-1.365029720	-12.847236960
H	0.500981510	-1.901003350	-12.245301990
H	-2.878713910	1.780242480	-11.584088610
H	-2.265013110	3.462431720	-11.521697200
H	-2.221181590	2.431541690	-10.067712910
H	-6.362033950	0.641073820	1.232158460
H	9.162300750	-4.309706790	2.882769870
O	0.958713750	5.489951650	-12.230316670
O	3.576407100	1.855301490	-14.280874420
O	1.294543410	3.360907300	-14.889099160
O	3.306663290	5.224396950	-13.738797010
H	0.482560020	2.849203390	-15.067874720
H	1.346574900	5.458597970	-11.316491640
H	3.149096180	1.084974560	-13.821989480
H	4.111378980	5.608869960	-13.341577920
H	2.587739230	5.874698340	-13.573502140
H	4.397406380	1.996774200	-13.752106220
H	2.022598620	2.877172560	-15.339866630
H	0.119568770	4.980818620	-12.129457630
Tb	2.008854610	-1.722092970	-4.001777790
H	-0.682663290	-1.374694680	-4.923029760
H	4.742339470	-1.158217080	-4.625204010
H	2.544159080	-4.463704530	-4.698092660
H	1.421559340	0.264170680	-2.032410970

Cartesian coordinates (in Å) for [Tb₂2₂(H₂O)₆]-**(VI)** optimized at the PBE/L1 level

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Complex structure (VI)

C	-2.34171440	-7.76048692	-11.14796167
C	-3.29651757	-7.01785262	-10.43793199
C	-2.94019454	-6.23244109	-9.33771508
C	-1.58803701	-6.14637708	-8.92785680
C	-0.62223775	-6.90248335	-9.63070014
C	-1.00854303	-7.69097846	-10.71897001
S	-4.21878414	-5.44420837	-8.34176912
C	-3.96749900	-3.71541149	-8.79600531
C	-3.38967378	-2.78178072	-7.90647301

C	-3.26396435	-1.43790816	-8.34526145
C	-3.63128582	-1.07582559	-9.64269882
C	-4.17059674	-2.00665828	-10.54105849
C	-4.37309794	-3.30613093	-10.06784758
S	1.06005761	-7.00124848	-9.00342027
C	1.67752829	-5.30921183	-9.12305784
C	2.25403031	-4.89151495	-10.32294260
C	2.87800508	-3.64541798	-10.46297671
C	2.93580585	-2.83533863	-9.32321625
C	2.32366326	-3.20941095	-8.12938521
C	1.66481384	-4.46176882	-7.96557884
O	-1.29352102	-5.37346529	-7.88773801
S	-2.81879388	-0.16457315	-7.14328275
C	-1.04042575	-0.00750999	-7.36511449
C	-0.54976621	1.14357009	-7.98196116
C	0.81923626	1.36930545	-8.18227864
C	1.68857789	0.34421419	-7.79172060
C	1.21308305	-0.81666703	-7.17734224
C	-0.16509174	-1.01942390	-6.86666843
C	-4.57224146	-1.62320400	-11.95923845
C	-3.42472547	-1.58558623	-12.97068097
C	-2.89643923	-0.33673443	-13.38795848
C	-3.52608425	0.96827221	-12.93685918
O	-3.00352404	-3.15924017	-6.67745988
S	2.40051879	-2.09004235	-6.71988015
Tb	0.59653362	-3.59280643	-4.94542372
C	1.28768648	2.65558647	-8.83604542
C	2.57211805	3.31115186	-8.26290904
C	2.65159642	3.27439989	-6.70843290
C	1.39536892	3.72838395	-5.99280793
O	-0.59226519	-2.05029114	-6.17754738
C	3.50926288	-3.21300237	-11.77880884
C	2.52128324	-2.69951102	-12.82804091
C	2.13153649	-3.53722428	-13.90448456
C	2.78565526	-4.88830607	-14.12308963
O	1.07922743	-4.81263100	-6.84471006
C	-2.69014273	-8.59252832	-12.36795474
C	-4.05501689	-9.32623796	-12.35584691
C	-4.38798209	-10.00194194	-10.99588400
C	-3.26278817	-10.82845233	-10.40459904
S	2.50049158	0.73080241	-0.66572017
C	3.61368447	-0.69405397	-0.44435582
C	3.89552714	-1.17490451	0.83887269
C	4.59875875	-2.37178936	1.04942051
C	5.09119262	-3.03409853	-0.07952919
C	4.87310516	-2.55803823	-1.36804541
C	4.13160737	-1.37590851	-1.56946164
C	4.70896552	-3.07245338	2.39846877
C	5.48175004	-2.30561244	3.46789142
C	6.89748125	-2.31588606	3.51974261
C	7.74112664	-3.04468094	2.50868827
S	5.43078364	-3.46042066	-2.83112376
C	4.41670510	-4.94707817	-2.68678149
C	4.95848697	-6.04081729	-2.01238947
C	4.21457080	-7.20415517	-1.76917074
C	2.88250694	-7.21377142	-2.20073890
C	2.32109460	-6.12777210	-2.86997362
C	3.08065128	-4.96590834	-3.20776950

C	4.78381705	-8.38910890	-1.01487912
C	6.11018420	-9.00168247	-1.54901843
C	6.16997707	-9.08912823	-3.09571361
C	4.97944193	-9.76705132	-3.74601854
S	0.60721935	-6.18005856	-3.41710021
C	-0.27978455	-5.48077593	-1.98832438
C	-0.37485701	-6.23195174	-0.81881130
C	-1.05400330	-5.75474976	0.30922266
C	-1.63894724	-4.48921108	0.21672808
C	-1.54018701	-3.71108423	-0.93753837
C	-0.90561944	-4.19558002	-2.12167468
C	-1.11038370	-6.58194744	1.59272686
C	-2.21727162	-6.21653192	2.55690591
C	-1.98757007	-5.41366998	3.67876256
C	-0.64622022	-4.85663364	4.07210213
S	-2.23982274	-2.03967496	-0.93118764
C	-1.01484443	-1.19661353	0.09037258
C	-0.98186609	-1.34599326	1.47349151
C	-0.03754989	-0.67186108	2.25854130
C	0.94866978	0.06409093	1.58759842
C	1.01987341	0.13699170	0.18612644
C	-0.05065590	-0.39239160	-0.56919859
O	-0.13463254	-0.17898096	-1.89869962
O	-0.92063672	-3.52555537	-3.24377473
O	2.55910350	-3.99064268	-3.89794018
O	3.88957546	-0.93039842	-2.83233300
C	-0.03916605	-0.81089479	3.76882300
C	-1.40644809	-0.51593071	4.42664793
C	-1.62115700	-1.38847491	5.69365770
C	-2.81606750	-1.05790441	6.55985326
C	4.81246041	-1.51380177	4.44321075
C	3.34088527	-1.25386017	4.51189194
C	7.35635218	-8.35643256	-0.91009015
C	8.68633588	-8.98921317	-1.24761790
C	-1.53786572	0.99234161	4.73643224
C	-2.74560712	1.69771548	4.15677402
C	-3.56751841	-6.66142334	2.33370178
C	-3.90052366	-7.52704169	1.14028596
O	5.49820189	-0.93022425	5.36811235
O	7.53130573	-1.67906196	4.44500906
O	7.26757709	-7.40572392	-0.15446703
O	7.09526264	-8.65952470	-3.75470689
O	-0.68526714	1.57038949	5.38022630
O	-0.87094053	-2.30962016	5.94252362
O	-4.51187807	-6.34928014	3.12279228
O	-2.97390587	-5.07756057	4.48604624
C	2.04362086	-1.36553057	-12.73896970
C	2.55106587	-0.41290710	-11.69234763
C	3.85107890	2.82740852	-8.97267367
C	5.13709483	3.51580023	-8.58674922
C	-5.18668957	-8.46333377	-12.95190141
C	-6.54281714	-9.11455456	-13.06958212
C	-2.94309973	-2.79946274	-13.53065948
C	-3.59952421	-4.12250036	-13.24087682
O	1.15858248	-0.86192283	-13.53831064
Tb	-0.28480550	-1.54067942	-15.13761849
O	-1.61966220	-1.05676758	-17.20889401
O	1.23136619	-3.23266381	-14.77860825

O	3.81634146	1.94986656	-9.81825456
O	3.64498426	2.93439401	-6.09984502
O	-4.97938829	-7.32594601	-13.33745620
O	-5.46522031	-9.90697920	-10.44399714
O	-1.92865842	-2.86910059	-14.33081303
O	-1.88716426	-0.19709055	-14.17994332
O	-0.73188094	-3.64711387	-16.56315336
O	0.28584351	0.97934891	-15.22845613
O	1.34293994	-0.96583924	-16.96042372
H	-1.72442451	-1.99661929	1.94269948
H	1.72786478	0.56700753	2.16594955
H	0.10166327	-7.21740846	-0.78753016
H	5.98533439	-5.97564028	-1.64616155
H	2.25559981	-8.09085645	-2.00673802
H	3.51722124	-0.61028390	1.68992413
H	5.64029778	-3.97208286	0.04255628
H	-2.19486284	-4.10056712	1.07282042
H	4.01511723	-9.17678505	-0.97323560
H	4.99920801	-8.08540069	0.02439419
H	0.70359724	-0.15997162	4.26002362
H	0.21566731	-1.84978807	4.03983178
H	-0.13826196	-6.49483637	2.10818357
H	-1.19572916	-7.64798258	1.31606001
H	5.20004858	-4.04453685	2.22358802
H	3.69668314	-3.31561855	2.76398018
H	6.13772825	-10.06176480	-1.21992238
H	-2.23314142	-0.80539383	3.75137125
H	-3.55744378	-7.05588268	0.20566709
H	-4.98658883	-7.68354612	1.10929631
H	-3.39505203	-8.50430241	1.21813410
H	-0.81058163	-3.97581121	4.71449999
H	-0.06096919	-4.55785828	3.18964183
H	-0.06340155	-5.60796306	4.62963173
H	-2.68725480	-0.05486072	6.99977853
H	-2.90950483	-1.80269163	7.36054540
H	-3.73758108	-1.03886731	5.95549561
H	-3.67777821	1.17192573	4.42045181
H	-2.66776876	1.67343204	3.05538321
H	-2.78140047	2.73931033	4.50266968
H	4.66370457	-10.66141152	-3.18597995
H	5.23430066	-10.02661676	-4.78214113
H	4.13071678	-9.06217702	-3.75449734
H	8.88893899	-8.78115621	-2.31117125
H	8.64962736	-10.08484342	-1.13258511
H	9.47240465	-8.56125102	-0.61223780
H	2.93697149	-1.00589096	3.52305914
H	3.12938849	-0.42047663	5.19691272
H	2.79791069	-2.15043869	4.85639535
H	7.57792013	-4.13353039	2.57252642
H	8.79876405	-2.82895839	2.70972302
H	7.48432055	-2.73351863	1.48438608
H	-4.35001829	-7.04494216	-10.72376793
H	-0.23706142	-8.27073518	-11.23618984
H	-3.52357398	-0.02499712	-9.92557647
H	2.76326284	0.43443625	-7.96501451
H	-1.27724582	1.89545431	-8.30537339
H	2.23057503	-5.59383168	-11.16099040
H	3.47343478	-1.88369183	-9.35236460

H	-4.86377413	-4.05003585	-10.69960649
H	0.46224727	3.38379487	-8.79057289
H	1.49832948	2.46909178	-9.90449164
H	-1.88349018	-9.32454969	-12.53220067
H	-2.71782155	-7.93426042	-13.25487434
H	-5.06726307	-0.64202794	-11.93275102
H	-5.34494439	-2.33180646	-12.30093543
H	4.07489823	-4.05978478	-12.19378124
H	4.26251596	-2.43705208	-11.56472800
H	2.51927985	4.39743410	-8.48794126
H	-3.96977300	-10.18818961	-13.05154746
H	-3.23226471	-4.51558362	-12.27673682
H	-3.32768181	-4.84764987	-14.01943999
H	-4.69429508	-4.06157365	-13.17145714
H	-3.06615949	1.79395262	-13.49746401
H	-3.35012030	1.13577610	-11.86200096
H	-4.61486812	0.98750332	-13.09928573
H	-3.65661954	-11.42687978	-9.57274628
H	-2.47737500	-10.15292525	-10.02658058
H	-2.80233924	-11.47929991	-11.16529737
H	-7.22301792	-8.46081870	-13.63065511
H	-6.91620670	-9.29421031	-12.04776369
H	-6.46739301	-10.10098778	-13.55640180
H	0.97910056	4.64040577	-6.44999542
H	1.62836390	3.89708652	-4.93331883
H	0.62928656	2.93895271	-6.07260547
H	5.35382299	3.24572616	-7.53966449
H	5.02692299	4.61228983	-8.61744312
H	5.94848595	3.19204131	-9.25132416
H	2.03121938	-0.60232332	-10.73695417
H	2.32793936	0.61859743	-11.99468931
H	3.62775895	-0.50372063	-11.49614318
H	3.88325399	-4.84311463	-14.05898075
H	2.49758329	-5.26274345	-15.11543338
H	2.44098354	-5.61245941	-13.36680257
H	-3.83231481	-5.57053144	4.04965361
H	6.63293398	-1.20846742	5.06190467
H	2.27714777	-1.21191153	-16.81887562
H	-1.37670973	-3.88494177	-15.84751105
H	0.80914214	0.79219178	-14.40614218
H	-2.57434129	-0.88582976	-17.09649141
H	-1.55110392	-1.94297923	-17.62861409
H	-0.61274025	1.18357486	-14.87394568
H	1.30502070	0.01285445	-16.87639743
H	0.11449268	-4.03704052	-16.23681164
H	-0.34625327	-5.46744286	-7.55305608
H	4.33368402	-1.60696806	-3.41779289
H	-0.85964283	-0.79831965	-2.20514651
H	-2.28690272	-2.52140271	-6.36126152
O	1.29092366	-1.84518298	-3.41709245
H	1.20341425	-0.87830585	-3.28588785
H	2.24929965	-2.03208606	-3.31502799
O	-1.47403239	-5.01333858	-5.27814099
H	-2.07315787	-4.75752587	-6.01854919
H	-1.86741273	-4.62693955	-4.46229615

Cartesian coordinates (in Å) for [Tb₂2(H₂O)₆]-**(VII)** optimized at the PBE/L1 level

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Complex structure (VII)

C	0.524592460	4.507921550	-4.748933930
C	1.859279240	4.145244700	-4.512653470
C	2.252674930	2.808390700	-4.417602850
C	1.306659100	1.757068370	-4.579830110
C	-0.031835840	2.125933580	-4.859798240
C	-0.401132880	3.475152420	-4.931157030
S	3.933543160	2.455679580	-3.902241670
C	4.581590650	1.488946080	-5.278721370
C	4.837935770	0.098675430	-5.119262680
C	5.422231630	-0.580256950	-6.218243110
C	5.771750750	0.115930150	-7.379467980
C	5.508237640	1.478664480	-7.541410420
C	4.913367420	2.144414260	-6.460873100
S	-1.331329500	0.885424800	-4.929991190
C	-0.992699560	-0.007974670	-6.456797680
C	-1.567440600	0.436475780	-7.646956200
C	-1.446372990	-0.269962500	-8.850692290
C	-0.790475130	-1.506350290	-8.800696290
C	-0.215141280	-1.979448850	-7.621629720
C	-0.230967590	-1.222659530	-6.406945350
O	1.733164290	0.507851890	-4.445169630
S	5.731326050	-2.359882220	-6.131063240
C	4.502686330	-2.920950620	-7.326818430
C	4.887145100	-3.092858560	-8.656570570
C	3.980577540	-3.435738110	-9.673139600
C	2.636064380	-3.567533950	-9.306086010
C	2.230763220	-3.433462650	-7.977338660
C	3.153806260	-3.178742280	-6.906298790
C	5.924153540	2.228263650	-8.799716900
C	4.832508530	2.458010750	-9.847775100
C	4.629171810	1.482011100	-10.866717660
C	5.458640590	0.219448940	-10.915120180
O	4.531601380	-0.452843580	-3.952023740
S	0.478556810	-3.641575760	-7.591801030
Tb	0.962277400	-3.749705660	-4.549628040
O	-1.574904650	-3.615829840	-4.777432540
C	4.458351470	-3.603657220	-11.101928840
C	3.940810790	-4.855405840	-11.863071890
C	3.899365750	-6.126932960	-10.973351330
C	5.198088930	-6.443007970	-10.258999200
O	2.805081310	-3.195273330	-5.660840230
C	-2.000908470	0.285078610	-10.153392270
C	-0.962030000	1.049927020	-10.974175400
C	-0.777592050	2.445147860	-10.747777680
C	-1.691324250	3.226954950	-9.829020420
O	0.372267560	-1.615639690	-5.322141220
C	0.076890170	5.953023350	-4.843337580
C	0.598440390	6.921741950	-3.745473120
C	0.622020770	6.297833610	-2.327381060
C	-0.661592370	5.617078370	-1.904843180
S	5.232400810	-0.891377770	-0.730683880
C	5.146457910	-2.671581020	-0.495440250
C	5.167272740	-3.212279970	0.792440990
C	5.176143760	-4.593276420	1.022822980

C	5.184708930	-5.437972390	-0.089453550
C	5.144051220	-4.924572500	-1.386278180
C	5.111681050	-3.532804660	-1.613838660
C	5.227092130	-5.164955930	2.433468650
C	4.157111580	-4.658504270	3.379551810
C	4.456495030	-3.791953440	4.433648750
C	5.836436640	-3.275409470	4.745059630
S	5.119840130	-6.024127060	-2.812280400
C	3.505635940	-6.778308230	-2.602398510
C	3.433305460	-8.162014050	-2.441823190
C	2.203909200	-8.828301330	-2.337770630
C	1.045079780	-8.044224910	-2.281018320
C	1.097351080	-6.663298020	-2.466610290
C	2.323873180	-5.979536410	-2.734865420
C	2.103739870	-10.320785220	-2.541359000
C	2.157571520	-10.696470280	-4.065462250
C	1.424470710	-9.622152460	-4.877781930
C	-0.070470030	-9.795121870	-5.013738630
S	-0.442159550	-5.766754200	-2.686201730
C	-0.522792070	-4.625157380	-1.288912920
C	-0.911627420	-5.085849610	-0.028563710
C	-1.070966060	-4.210984560	1.051838790
C	-0.867721110	-2.844818580	0.815251660
C	-0.485884540	-2.362176720	-0.435319360
C	-0.284594940	-3.246903590	-1.536569770
C	-1.442409370	-4.726973420	2.436576040
C	-2.537560040	-3.955533520	3.145213520
C	-2.283062220	-3.040501780	4.172434170
C	-0.927650660	-2.680113080	4.707647720
S	-0.340881620	-0.584863120	-0.720320440
C	1.262421680	-0.176928790	-0.022488640
C	1.335631000	0.803698440	0.971916240
C	2.564975510	1.263794980	1.457143290
C	3.727098140	0.654226010	0.965649470
C	3.681615100	-0.322576570	-0.035097500
C	2.440186350	-0.720161280	-0.587322650
O	2.429249680	-1.588876190	-1.607606170
O	0.091168560	-2.789884080	-2.719065090
O	2.354019940	-4.735876970	-3.113091390
O	5.047707290	-3.040079830	-2.872814250
C	2.625555050	2.424985380	2.420609890
C	2.717839260	3.774796030	1.676465320
C	2.234583810	4.951396650	2.554825230
C	2.326518160	6.326000220	1.919604390
C	2.785519070	-5.069388920	3.231681200
C	2.382725540	-6.006358920	2.121052320
C	3.607458130	-10.961707910	-4.539821850
C	3.809298500	-11.100449360	-6.033831830
C	4.161808150	4.025168180	1.177807690
C	4.326290410	4.283853830	-0.301350810
C	-3.916755940	-4.147503450	2.767958920
C	-4.277795260	-5.122721690	1.668934730
O	1.882738580	-4.661773410	4.029869430
O	3.523791670	-3.370881140	5.261536540
O	4.519510270	-11.101628300	-3.751438280
O	2.017563730	-8.668660990	-5.365119640
O	5.099639550	3.977416150	1.950517120
O	1.790677150	4.781958260	3.671723690

O	-4.863106910	-3.524787690	3.334817200
O	-3.266533390	-2.392554960	4.765708820
O	1.188734330	-5.968759860	-5.693477300
C	-0.184789450	0.380650840	-11.950088440
C	-0.459396580	-1.030419630	-12.412445060
C	2.643165830	-4.572685790	-12.644227170
C	2.085446250	-5.712138980	-13.461747560
C	1.905387110	7.629941110	-4.165093170
C	2.437999760	8.682660460	-3.221617350
C	4.047883080	3.634964390	-9.822652550
C	4.250504450	4.739008950	-8.811950620
O	0.817621390	0.930100670	-12.559618780
Tb	2.045275840	2.866157760	-12.439878100
O	3.678000560	4.196138110	-13.831403510
O	0.144707720	3.157983920	-11.291662890
O	2.115537880	-3.472997180	-12.626308170
O	2.915708410	-6.828673630	-10.848227820
O	2.448730010	7.378950660	-5.225182410
O	1.588843920	6.354370470	-1.588675440
O	3.074985830	3.864874440	-10.649425340
O	3.750258880	1.572192770	-11.802115070
O	1.883963510	5.463356930	-12.225242100
O	2.395273280	1.300475800	-14.513183900
O	0.831852160	3.511562860	-14.557412440
H	0.401456860	1.217648150	1.363722730
H	4.706007840	0.953856750	1.351736900
H	-1.095080660	-6.157154910	0.106650330
H	4.361608100	-8.740677920	-2.449774880
H	0.065570640	-8.515943750	-2.149116860
H	5.167864290	-2.515181870	1.635109770
H	5.215177150	-6.523641170	0.043124290
H	-1.022665350	-2.125094590	1.623303550
H	1.167705550	-10.706527730	-2.107443300
H	2.952389950	-10.850776210	-2.078089320
H	3.503732500	2.349976680	3.082259440
H	1.732593090	2.455887040	3.064726860
H	-0.532362010	-4.737660130	3.059890150
H	-1.739618140	-5.786028590	2.336726970
H	6.218042270	-4.956195490	2.869590400
H	5.169229460	-6.265402770	2.357118250
H	1.625871650	-11.658723710	-4.207448480
H	2.049084860	3.764259200	0.794723670
H	-3.749396180	-4.873789000	0.734894880
H	-5.363595270	-5.086629970	1.510514680
H	-3.982838710	-6.148774700	1.945805390
H	-0.970445550	-2.688055030	5.808033470
H	-0.684092310	-1.647688480	4.404226890
H	-0.125928830	-3.343880460	4.366187320
H	3.389833870	6.604419770	1.818111680
H	1.821805840	7.062066950	2.559801580
H	1.895788040	6.324602280	0.904676620
H	3.616415470	5.046405020	-0.659869530
H	4.085126660	3.350306550	-0.842422330
H	5.361849340	4.573702500	-0.525131290
H	-0.257474130	-10.574229500	-5.775451310
H	-0.543075200	-8.858032500	-5.339377800
H	-0.523927930	-10.147192560	-4.074826440
H	3.779050270	-10.091871290	-6.477076120

H	3.000000370	-11.686495490	-6.499037930
H	4.784816320	-11.562628340	-6.233027230
H	2.524454270	-5.523588100	1.140289550
H	1.327344660	-6.279931960	2.243267740
H	3.005532130	-6.915424790	2.122781670
H	6.470199410	-4.082395640	5.149210450
H	5.751471100	-2.484933040	5.502740180
H	6.335788880	-2.873253970	3.851852390
H	2.627395580	4.912975650	-4.395289860
H	-1.453210990	3.708888540	-5.124927290
H	6.285869910	-0.441332890	-8.166568290
H	1.876607540	-3.778801490	-10.062488120
H	5.945212630	-2.948202500	-8.902223580
H	-2.151817630	1.359866560	-7.609673240
H	-0.727906150	-2.135477850	-9.693179040
H	4.728682700	3.219911470	-6.504547470
H	5.559984110	-3.608549080	-11.103597770
H	4.131141880	-2.738205910	-11.705675730
H	-1.024393840	5.976519680	-4.854437260
H	0.426270470	6.383922600	-5.798495300
H	6.761783400	1.685138540	-9.263824970
H	6.347400060	3.200473020	-8.503612910
H	-2.855132630	0.939743580	-9.923520930
H	-2.419460280	-0.538381350	-10.750637910
H	4.686906260	-5.103152800	-12.647718440
H	-0.143618990	7.743279300	-3.652144960
H	3.502799670	4.628095150	-8.006734570
H	4.061464350	5.708922640	-9.298031770
H	5.243651740	4.753868020	-8.349031660
H	5.316435230	-0.257217750	-11.894530600
H	5.105921680	-0.475986430	-10.133512010
H	6.529701410	0.396654600	-10.740029180
H	-0.639808090	5.430232030	-0.823205390
H	-0.741512690	4.653621480	-2.436894410
H	-1.544090700	6.217691400	-2.176695240
H	3.271410160	9.217090500	-3.695583030
H	2.770058300	8.175059590	-2.301757710
H	1.644514110	9.389884760	-2.928492960
H	6.067681720	-6.316952020	-10.923283010
H	5.155424580	-7.468158660	-9.868044080
H	5.320100030	-5.741430170	-9.416079970
H	1.720515190	-6.476002850	-12.755020850
H	2.871252070	-6.191218760	-14.068518140
H	1.270807260	-5.350343040	-14.102448310
H	0.389123890	-1.680041180	-12.136758510
H	-0.501436480	-1.028565880	-13.514851350
H	-1.384739190	-1.469454140	-12.025465150
H	-2.734912910	2.885033230	-9.842296470
H	-1.644208140	4.287701550	-10.113089990
H	-1.320145010	3.137091980	-8.793106520
H	-4.142712040	-2.747271720	4.267360590
H	2.633507390	-3.843624410	4.892451890
H	-0.126279760	3.326438800	-14.583990310
H	2.291215830	5.257810800	-11.331732630
H	1.823367170	0.691762660	-13.957862610
H	4.599226460	4.227028250	-13.509287560
H	3.289317820	5.073870120	-13.606575570
H	3.276896460	0.885540430	-14.563667590

H	1.253096870	2.806453650	-15.104083270
H	0.985191510	5.800615130	-12.050292870
H	1.461388870	-6.884562570	-5.421009590
H	-1.812864090	-2.981709510	-5.484677750
H	1.609360670	-5.847777890	-6.567478030
H	-1.508529860	-3.053997210	-3.964447940
H	1.031736390	-0.190027350	-4.642776520
H	4.807142020	-3.806467880	-3.457649590
H	4.757208930	-1.414657950	-3.888555620
H	1.503897860	-1.690878270	-1.959435380

Cartesian coordinates (in Å) for [Tb₃2₂(H₂O)₈]-**(VIII)** optimized at the PBE/L1 level

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Complex structure (VIII)

C	1.716419510	4.791455080	-5.265137180
C	2.988220600	4.204056590	-5.253198250
C	3.139452670	2.824112100	-5.139026420
C	2.023000400	1.941643020	-5.043425660
C	0.749595950	2.541002640	-5.246552310
C	0.614200010	3.932801180	-5.316832680
S	4.802975000	2.211155760	-4.832635540
C	5.162379660	1.097666170	-6.200470930
C	5.174818730	-0.304136250	-5.929918850
C	5.599640560	-1.129500590	-7.013993980
C	5.984113800	-0.567409980	-8.232762500
C	5.933057790	0.809891130	-8.487849880
C	5.529714180	1.635495860	-7.432766120
S	-0.745956520	1.553470090	-5.195302370
C	-0.627977780	0.596246540	-6.716013420
C	-1.241748470	1.069245190	-7.879013970
C	-1.300812420	0.304556720	-9.048872710
C	-0.822490900	-1.010104150	-8.982220610
C	-0.212582560	-1.515873120	-7.831205010
C	-0.034299680	-0.686878560	-6.698231870
O	2.186464690	0.659993630	-4.741290850
Tb	3.708391770	0.127989140	-3.015646150
O	6.204792950	-0.063524290	-2.644991940
S	5.649449800	-2.924503350	-6.810502860
C	4.265555190	-3.314504700	-7.893312310
C	4.496126700	-3.618215680	-9.236491380
C	3.460281440	-3.807509610	-10.166825550
C	2.150960050	-3.640994590	-9.701000530
C	1.898955090	-3.375307780	-8.355065920
C	2.931792510	-3.279393710	-7.370767600
C	6.373649940	1.388835510	-9.826236210
C	5.256797030	1.735432730	-10.813292070
C	4.794733090	0.737521380	-11.720300540
C	5.410709390	-0.641374320	-11.743812500
O	4.859715990	-0.784273580	-4.751778210
S	0.200069220	-3.279611140	-7.780713490
Tb	0.832397050	-3.442553900	-4.831660600
O	-1.656647610	-3.239751150	-5.243303730
C	3.784803520	-4.128415040	-11.613390450
C	2.880532430	-5.174544620	-12.317415140
C	2.547480940	-6.393318270	-11.412278430
C	3.753712470	-7.059585770	-10.780784700

O	2.668487490	-3.198705550	-6.097048040
C	-1.862795820	0.877259250	-10.342117250
C	-0.772954450	1.351151950	-11.303028710
C	-0.269331450	2.678895020	-11.184657110
C	-0.885400290	3.670403200	-10.221363810
O	0.652988130	-1.119570150	-5.619199450
C	1.554009730	6.281969690	-5.076129100
C	2.047302040	6.795859430	-3.675335920
C	1.952712270	5.670659220	-2.636868340
C	0.607228090	5.452427990	-1.996212930
S	4.379022790	-0.049968100	-0.123269060
C	4.769574630	-1.815078810	-0.048145610
C	5.375050530	-2.302763720	1.111739210
C	5.866974650	-3.610859900	1.190639310
C	5.762619850	-4.411334220	0.050122420
C	5.156968350	-3.949785560	-1.123398670
C	4.624628500	-2.646235350	-1.179047580
C	6.530487300	-4.130297750	2.460260740
C	5.747185350	-3.874634230	3.730222980
C	6.131389680	-2.881682000	4.689691130
C	7.391176560	-2.058450180	4.524918930
S	5.195787220	-4.972809520	-2.604797780
C	3.649224930	-5.874409310	-2.468275040
C	3.717431820	-7.256506650	-2.267353610
C	2.570160180	-8.057317900	-2.248229770
C	1.334926780	-7.408821270	-2.335131660
C	1.247975810	-6.038118190	-2.574851800
C	2.408062030	-5.225633710	-2.727955470
C	2.642016890	-9.562864430	-2.314477330
C	2.755092660	-10.097107010	-3.786682010
C	1.808020970	-9.315466850	-4.697586610
C	0.397482740	-9.841929830	-4.810452900
S	-0.379995360	-5.394409040	-2.980368770
C	-0.763127160	-4.222931490	-1.666128070
C	-1.140164900	-4.686442620	-0.405674970
C	-1.498012330	-3.788198610	0.605614730
C	-1.489513770	-2.427541560	0.287988620
C	-1.112094890	-1.946006540	-0.966240890
C	-0.725968150	-2.839971250	-2.001942740
C	-1.915302060	-4.281047600	1.988277530
C	-1.697674050	-3.298183300	3.119878780
C	-0.418252560	-3.079315990	3.652719650
C	0.824564450	-3.753186740	3.158638510
S	-1.057778570	-0.161221940	-1.234711050
C	0.307375450	0.177837870	-0.114239840
C	0.053936490	0.550641690	1.206454030
C	1.070945070	0.730868080	2.154980130
C	2.384237200	0.503080620	1.729342050
C	2.666187870	0.137271630	0.409335420
C	1.643219680	-0.007734940	-0.581064450
O	1.923797930	-0.269522950	-1.830458570
O	-0.368856750	-2.432063350	-3.205365340
O	2.319860250	-3.963590690	-3.136594670
O	4.002662720	-2.197848260	-2.304869720
C	0.801371080	1.081926710	3.604689970
C	-0.522826290	1.808227940	3.881014530
C	-0.658918530	2.028667040	5.418453640
C	-2.000518080	1.673221630	6.022687570

C	4.591970550	-4.617513700	4.015491020
C	4.091627720	-5.724968510	3.133021170
C	4.227933160	-10.113173170	-4.271197760
C	4.446417670	-10.397856790	-5.741014060
C	-0.569773070	3.185255550	3.184932760
C	-1.952937380	3.752466290	2.920621190
C	-2.771320210	-2.515413150	3.659646810
C	-4.185131410	-2.656240760	3.137669160
O	3.882124890	-4.384486520	5.090272750
O	5.432304920	-2.669643970	5.731976220
O	5.149392330	-9.956590020	-3.497986390
O	2.172888440	-8.294966200	-5.268377310
O	0.443082790	3.781770140	2.882965670
O	0.275056230	2.441625980	6.070530820
O	-2.575490630	-1.670800270	4.594278750
O	-0.227927130	-2.219731790	4.627717990
O	3.318158170	2.281942410	-1.910583350
O	1.401958590	-5.644650380	-5.779648290
C	-0.271605900	0.489475860	-12.310816590
C	-0.908939110	-0.829351600	-12.679142210
C	1.663053220	-4.527269850	-13.003124580
C	0.746865160	-5.446798460	-13.768291200
C	3.478567970	7.385826010	-3.753550580
C	4.022136560	7.971565030	-2.470077120
C	4.707940310	3.039085200	-10.856482640
C	5.205694790	4.169302080	-9.983992790
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O	1.419391940	-6.798153950	-11.219658630
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O	3.845453780	0.907650800	-12.570663450
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O	1.053974920	3.138609190	-15.245704540
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H	7.529043480	-3.671375620	2.549472450
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H	-4.585659560	-3.657920150	3.365589090
H	1.574744610	-3.774269540	3.961983830
H	1.234260480	-3.179399950	2.308762710
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6. Parameters of three-exponential expansion fittings for the phosphorescence decay curves of Gd^{3+} complexes with the ligands **1**, **2** and **4**

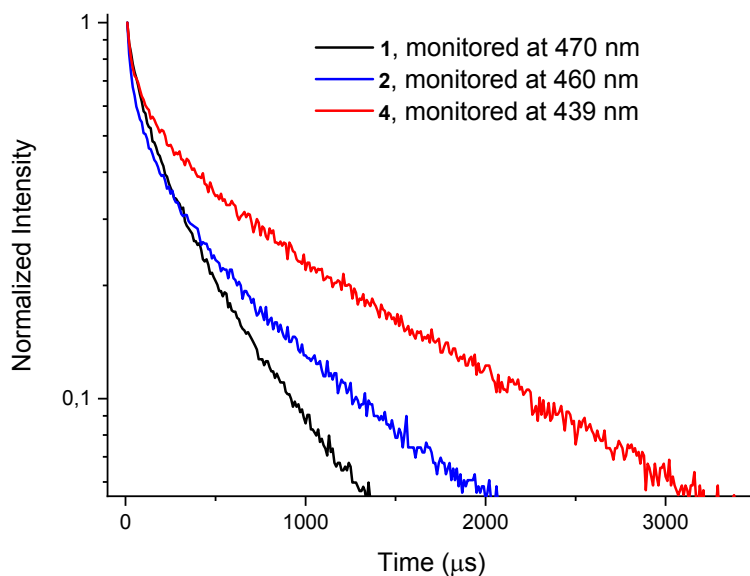


Figure S6. Normalized phosphorescence decay curves ($\lambda_{\text{exc}}=337$ nm) of the alkalized DMF solutions of Gd^{3+} complexes with the ligands **1** ($\lambda_{\text{max}}=470$ nm), **2** ($\lambda_{\text{max}}=460$ nm) and **4** ($\lambda_{\text{max}}=439$ nm) at $T=143$ K. $C_L = C_{\text{Gd}^{3+}} = 1$ mM, $C_{\text{TEA}} = 4$ mM.

The values of the lifetime (τ) of the Gd^{3+} complexes with the ligands **1**, **2**, and **4** were evaluated from the phosphorescence decay curves (Fig. S5) on the basis of three-exponential expansion:

$$I(t) = \sum_{i=1}^3 A_i \exp(-t / \tau_i) \quad (1)$$

where A_i and τ_i are the pre-exponential factors and decay times, respectively. The parameters A_i and τ_i are collected in Table S3. It is worth noting that the fitting of the decay curves with three-exponential expansion is characterized by notably smaller goodness-of-fit parameter χ^2 and regression coefficient R^2 values than those for single and double exponential expansions. Moreover, the fourth- and higher-order exponential expansions show no considerable improvement of the χ^2 and R^2 parameters. The intensity-weighted average phosphorescence decay time [1] was calculated using the equation 2 to characterize the decay curves for the Gd^{3+} complexes.

$$\langle \tau \rangle = \frac{\sum_{i=1}^3 A_i \tau_i^2}{\sum_{i=1}^3 A_i \tau_i} \quad (2)$$

Table S2. Parameters of three-exponential expansion fittings for luminescence decay curves of the Gd³⁺ complexes at 143 K (Normalized data).

Complex Gb ³⁺ - L	A ₁	τ ₁ (μs)	A ₂	τ ₂ (μs)	A ₃	τ ₃ (μs)	<τ> (μs)	Goodness-of- fit parameter χ ² , 10 ⁻⁶	R ²
1	0.3±0.005	40±1	0.5±0.005	247±5	0.2±0.01	905±15	633	6.4	0.9996
2	0.5±0.01	21±0.5	0.4±0.004	226±5	0.3±0.004	1185±14	971	12	0.9991
4	0.4±0.01	30±1	0.3±0.005	267±9	0.4±0.004	1601±19	1437	24	0.9989

1. J. R. Lakowicz, Principles of Fluorescence Spectroscopy, Kluwer Academic/Plenum, New York, USA, 2nd edition, 1999.

7. Normalized time-resolved luminescence spectra of the Tb^{3+} complex with the ligands 1, 2 and 4 at 300 K

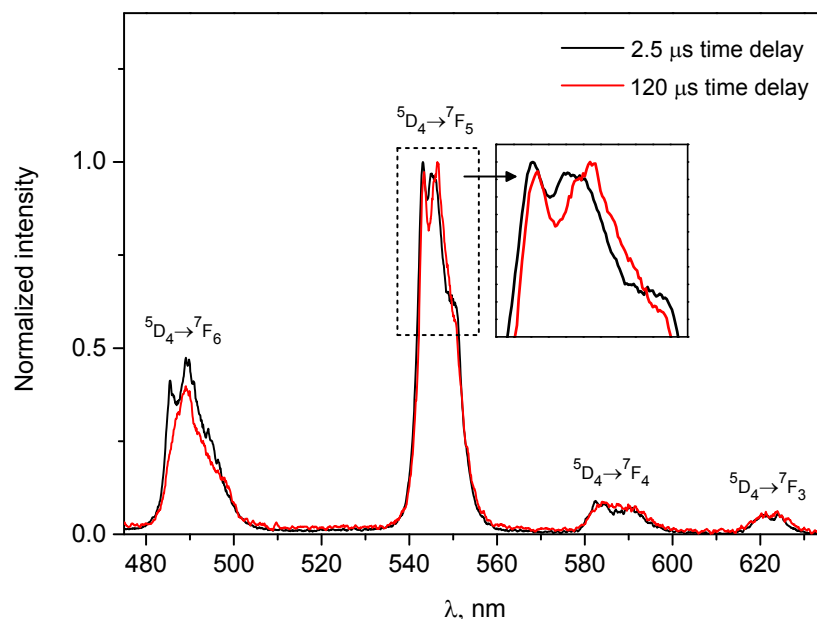


Figure S7. The normalized time-resolved luminescence spectra for the concentration ratio L(1-4): Tb^{3+} :TEA (1:1:8) in DMF under excitation at 337 nm by pulsed nitrogen laser (the time delays are 2.5 μs and 100 μs). $C_{\text{Tb}^{3+}} = C_{\text{L}} = 0.1 \text{ mM}$.

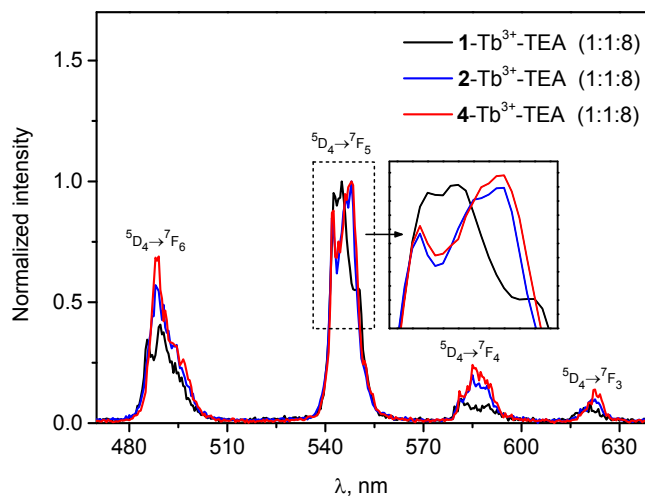


Figure S8. The normalized time-delayed luminescence spectra under excitation of a 337 nm pulsed nitrogen laser (the time delay is 2.5 μs for the concentration ratio L(1-4): Tb^{3+} :TEA (1:1:8) in DMF. $C_{\text{Tb}^{3+}} = C_{\text{L}} = 0.1 \text{ mM}$.

8. Luminescence decay curves of the Tb^{3+} complexes with the ligands 1, 2 and 4 at 300 K

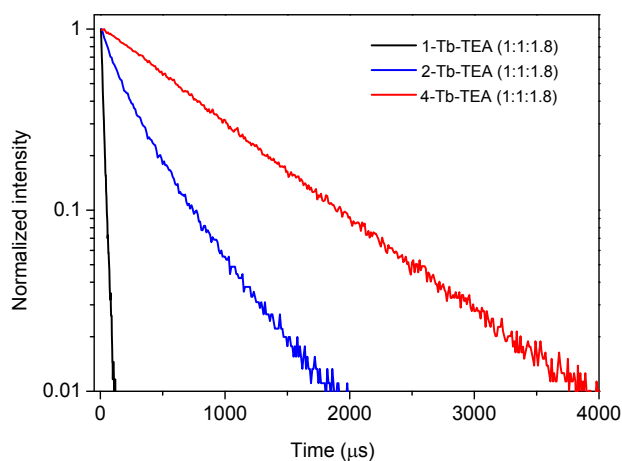


Figure S9. Normalized luminescence decay curves ($\lambda_{\text{ex}}=337$ nm, $\lambda_{\text{em}}=545$ nm) of the alkalinized DMF solutions of Tb^{3+} complexes with the ligands **1** ($\lambda_{\text{max}}=470$ nm), **2** ($\lambda_{\text{max}}=460$ nm) and **4** ($\lambda_{\text{max}}=439$ nm) at $T=143$ K. $C_{\text{L}} = C_{\text{Gd}^{3+}} = 1$ mM, $C_{\text{TEA}} = 4$ mM.

9. The luminescence titration of L-Tb^{3+} DMF solution at addition of TEA

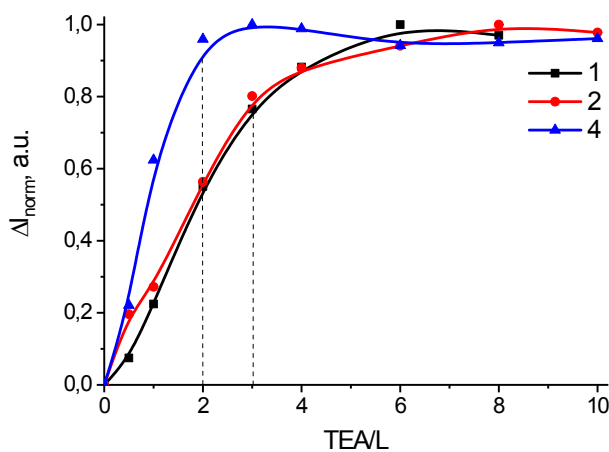


Figure S10. The normalized change of luminescence intensity in the DMF solution of L-Tb^{3+} -TEA at varied TEA:L molar ratios. The luminescence intensity at 545 nm for the Tb^{3+} complexes was registered at the maximum of excitation. $\text{L} = \mathbf{1}, \mathbf{2}$ and $\mathbf{4}$. $C_{\text{Tb}^{3+}} = C_{\text{L}} = 0.1$ mM.