Electronic Supplementary Information

Title: **A simple synthetic approach to enhance the thermal luminescence sensitivity of Tb^{3+} complexes with thiacalix[4]arene derivatives through upper-rim bromination**

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Content

1. Structural formulae of the investigated compounds 1, 2, 4-7

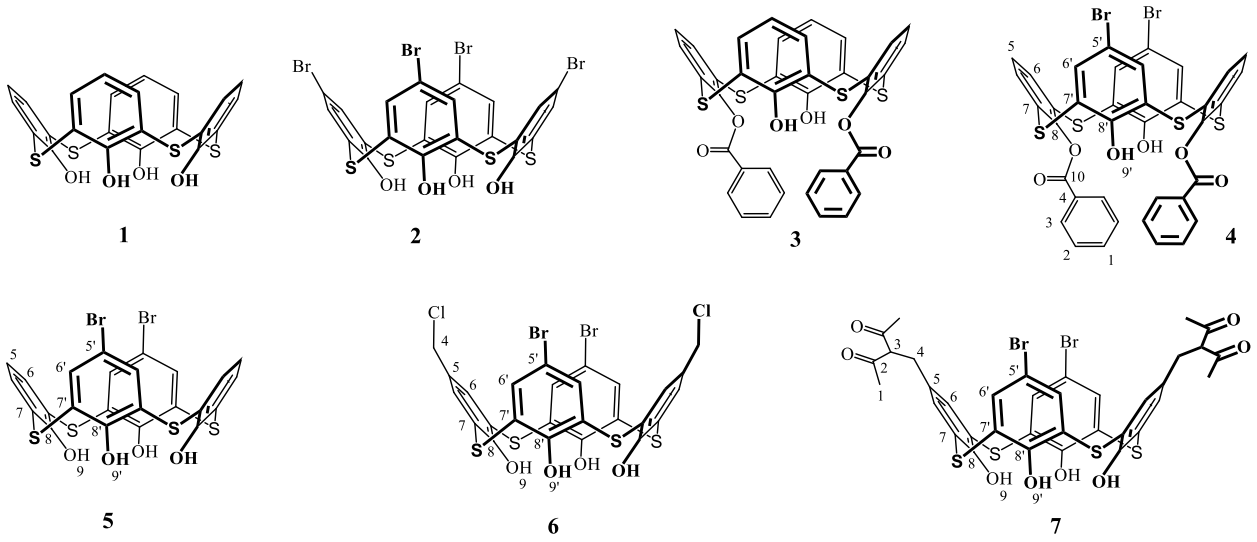


Figure S1. Structural formulae of the investigated compounds **1-7.** The same numbering system of atoms for the compounds was used in the Table S1.

2. IR spectra of compounds 1, 2, 5 and 7.

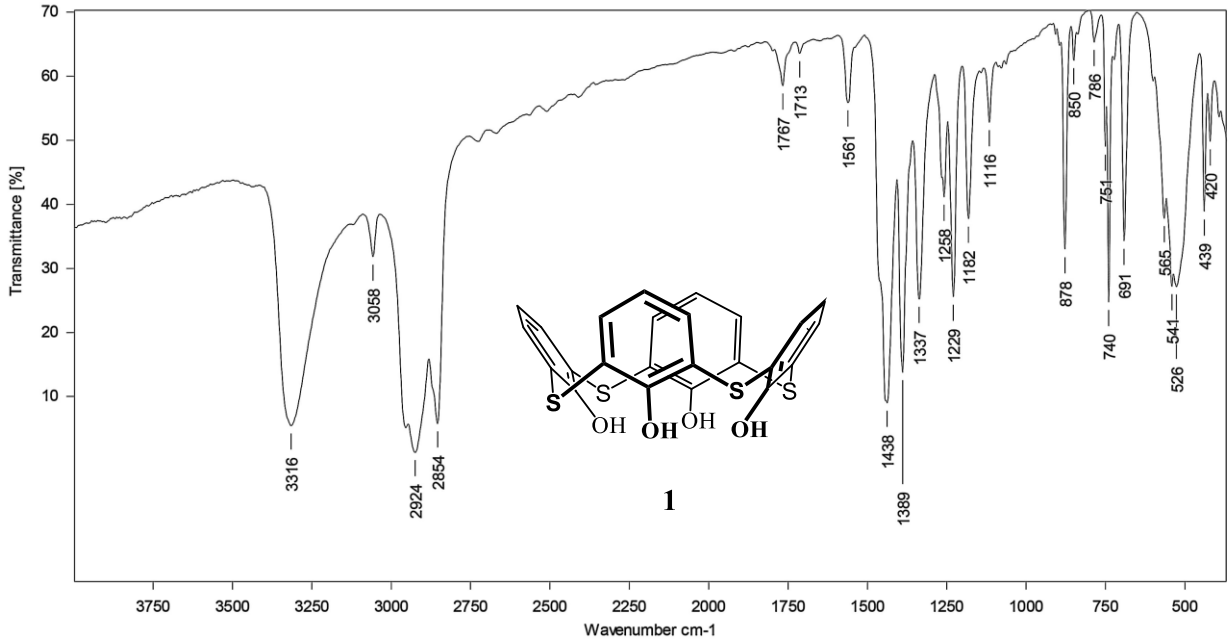


Figure S2. IR spectrum of compound **1** in Nujol.

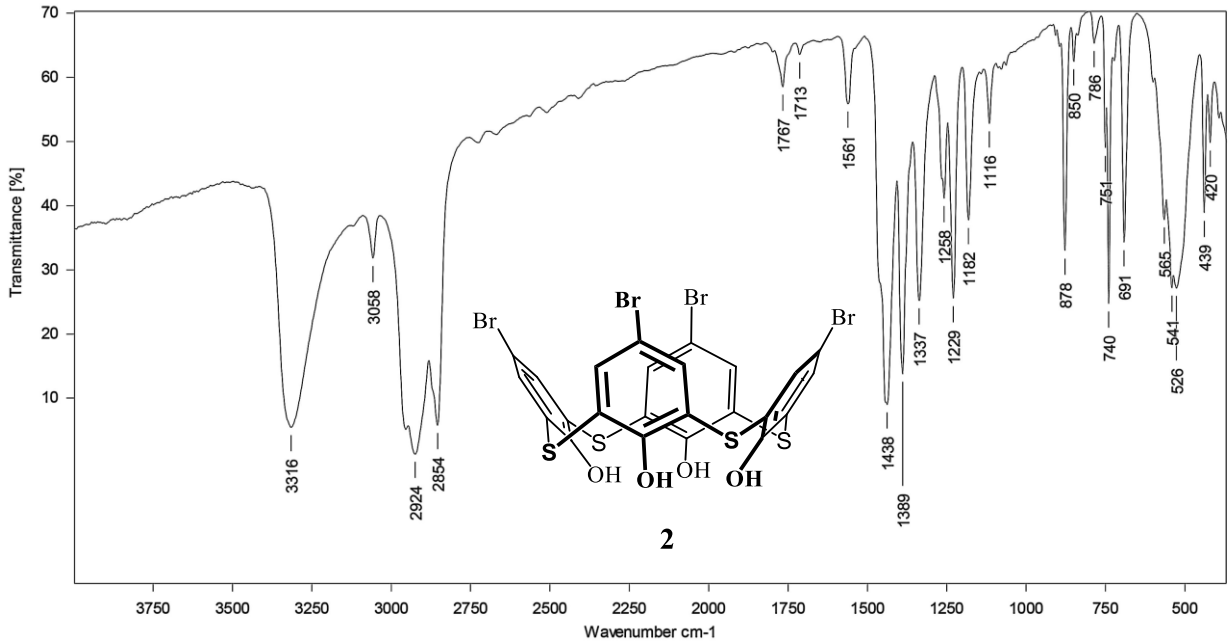


Figure S3. IR spectrum of compound **2** in Nujol.

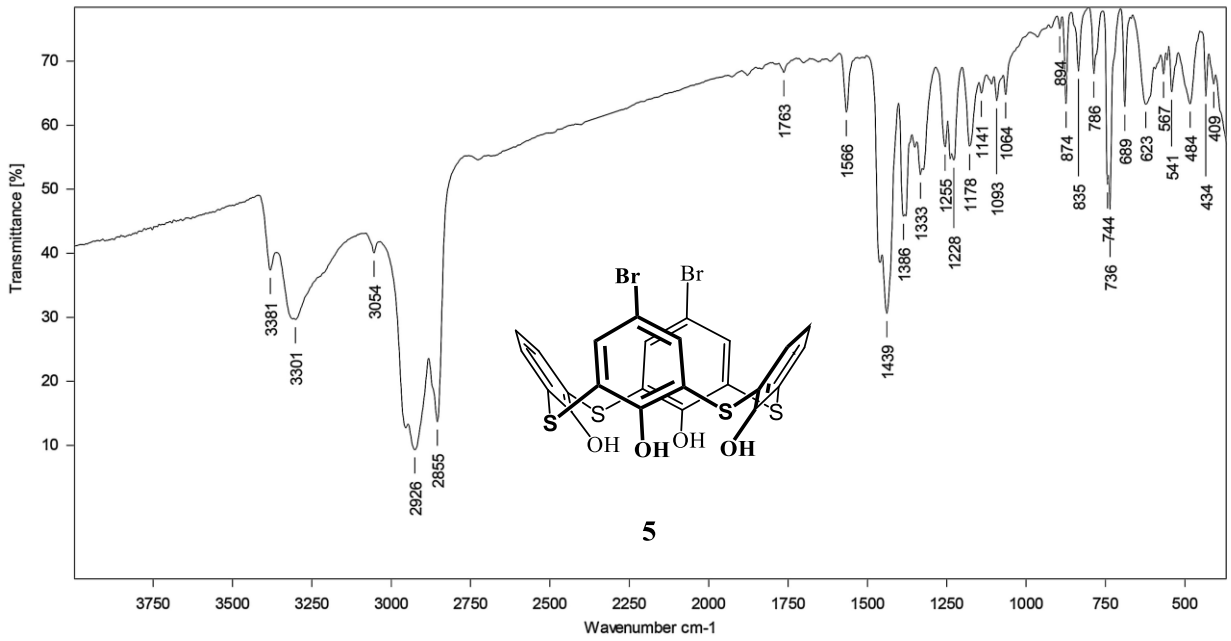


Figure S4. IR spectrum of compound **5** in Nujol.

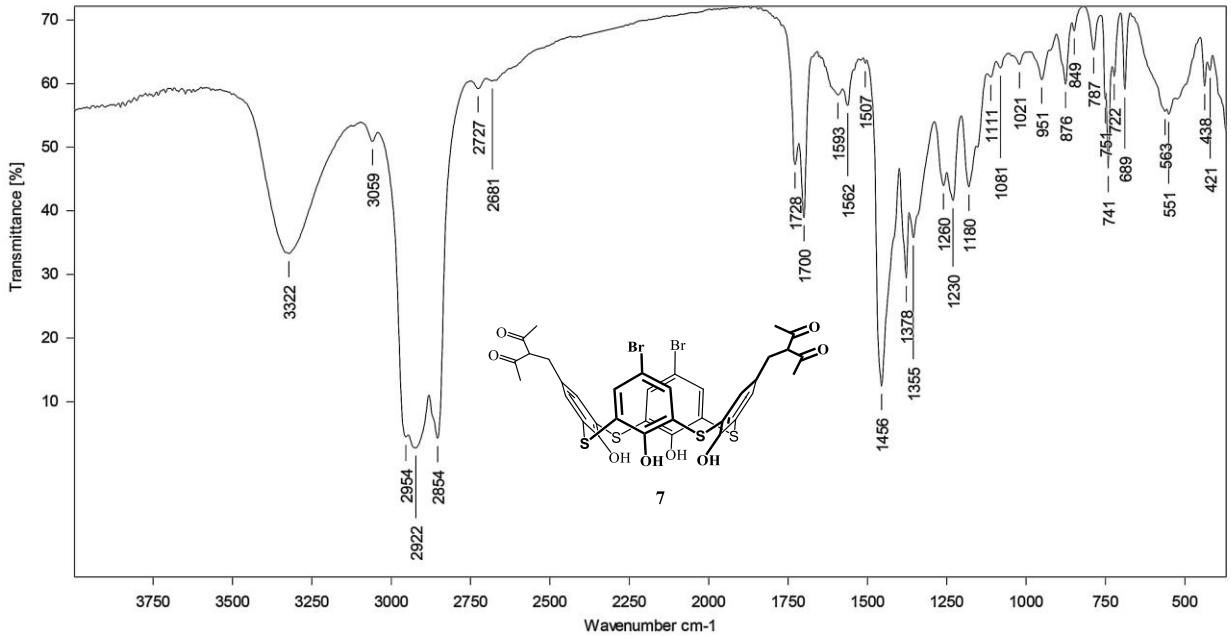


Figure S5. IR spectrum of compound **7** in Nujol.

3. ^{1}H NMR and ^{13}C NMR spectra of new compounds 4-7.

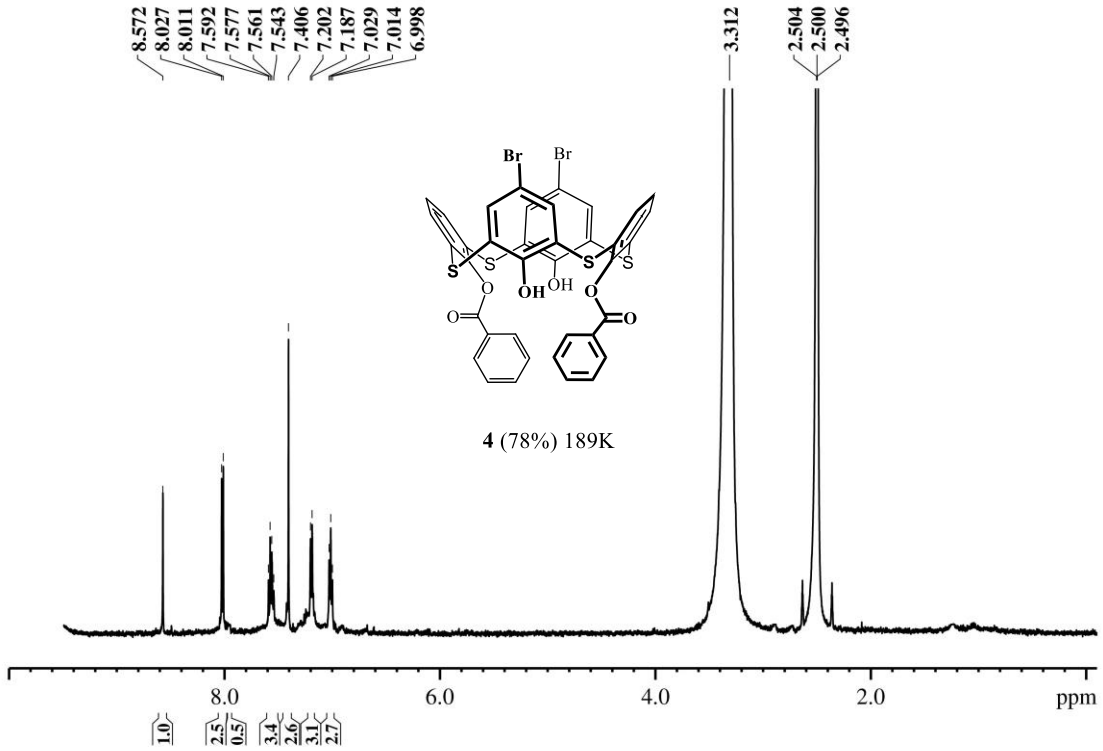
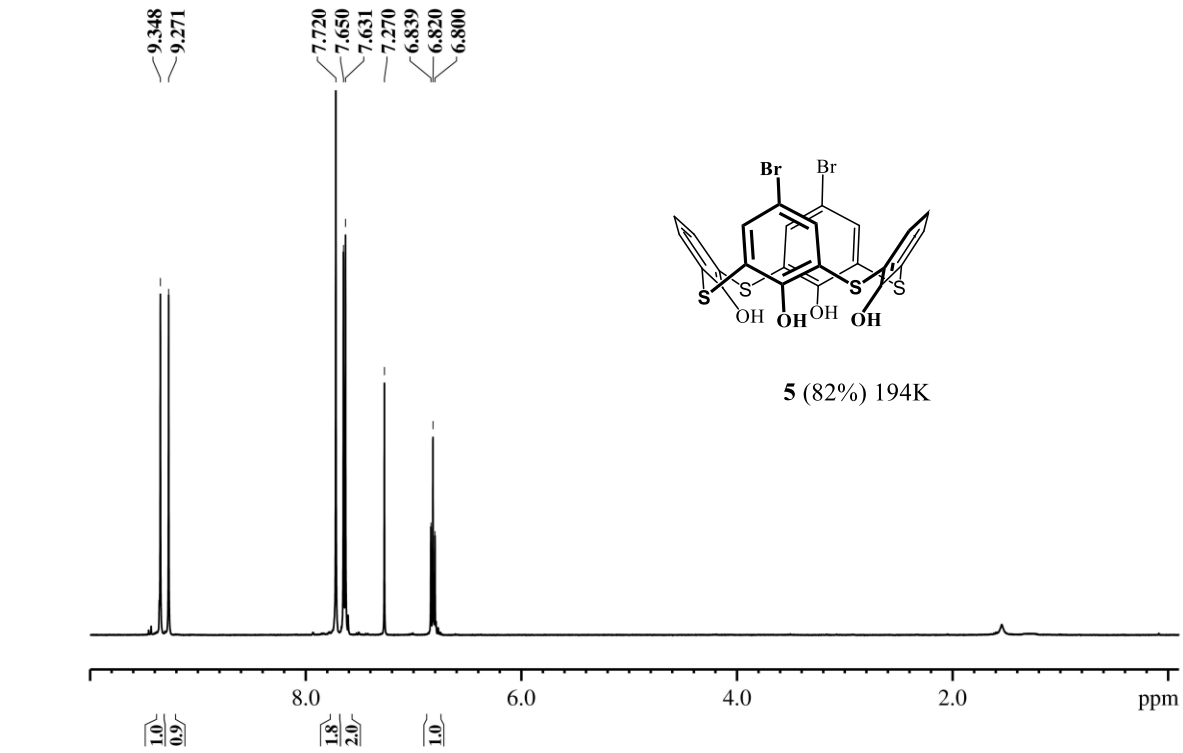
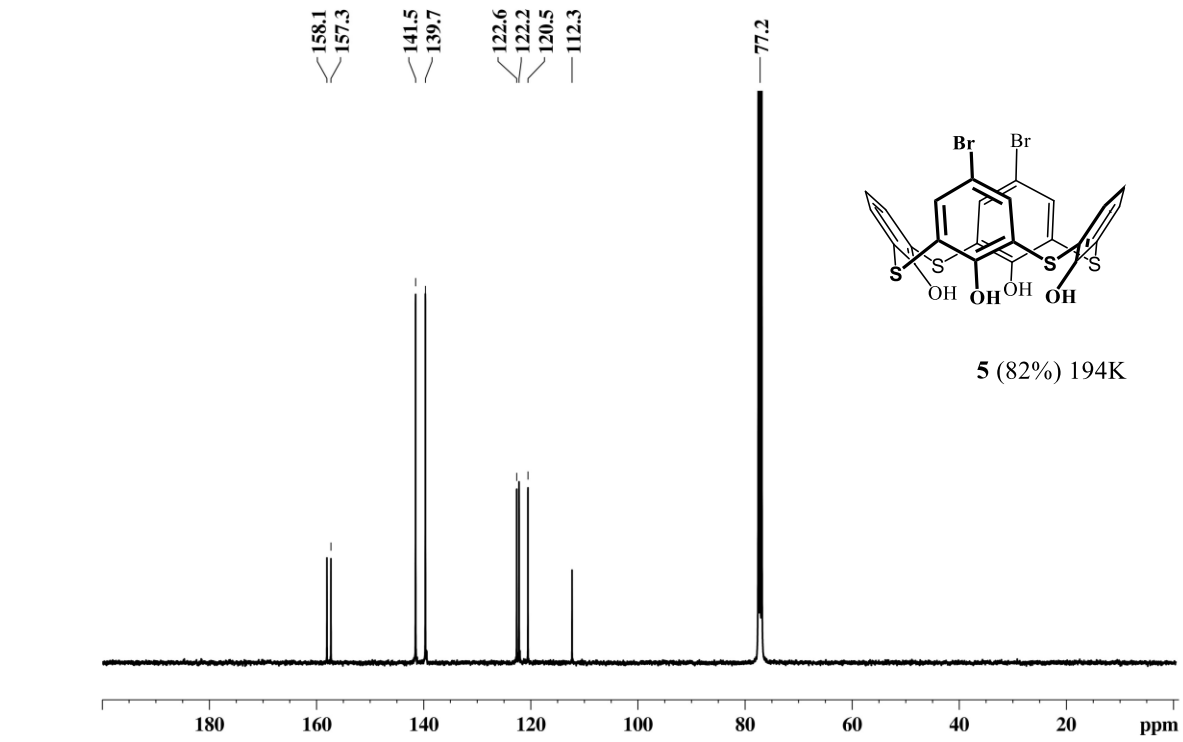


Figure S6. ^{1}H NMR spectrum (DMSO-d_6) of **4**.

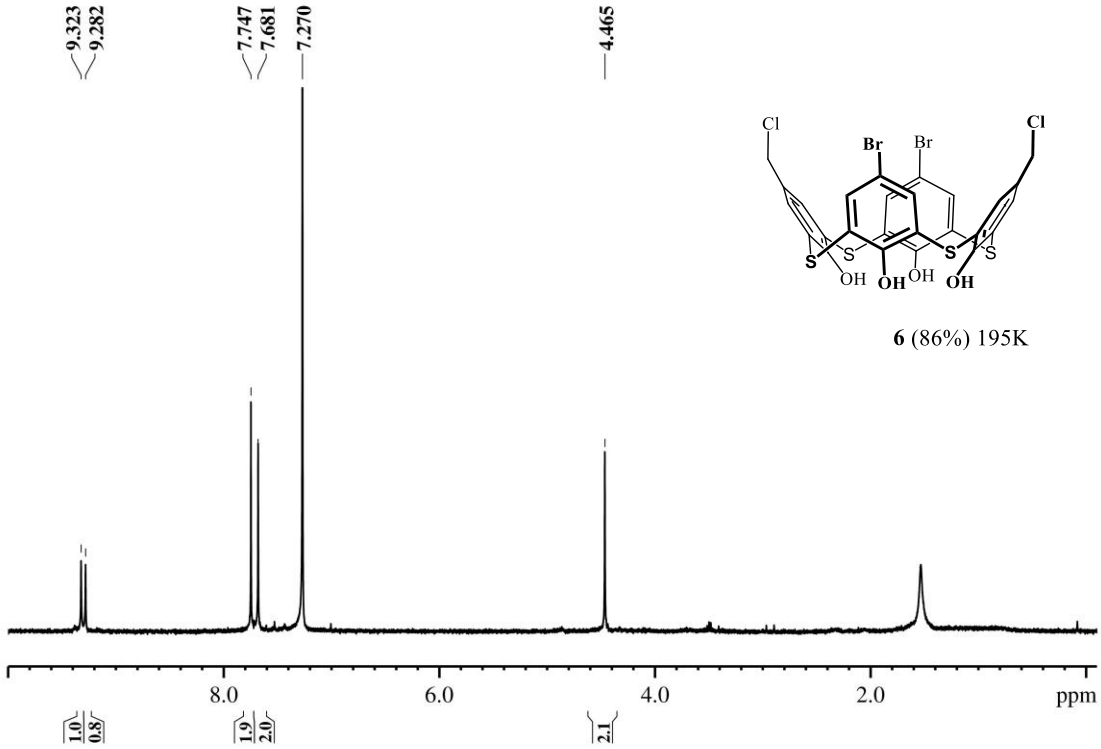


a)

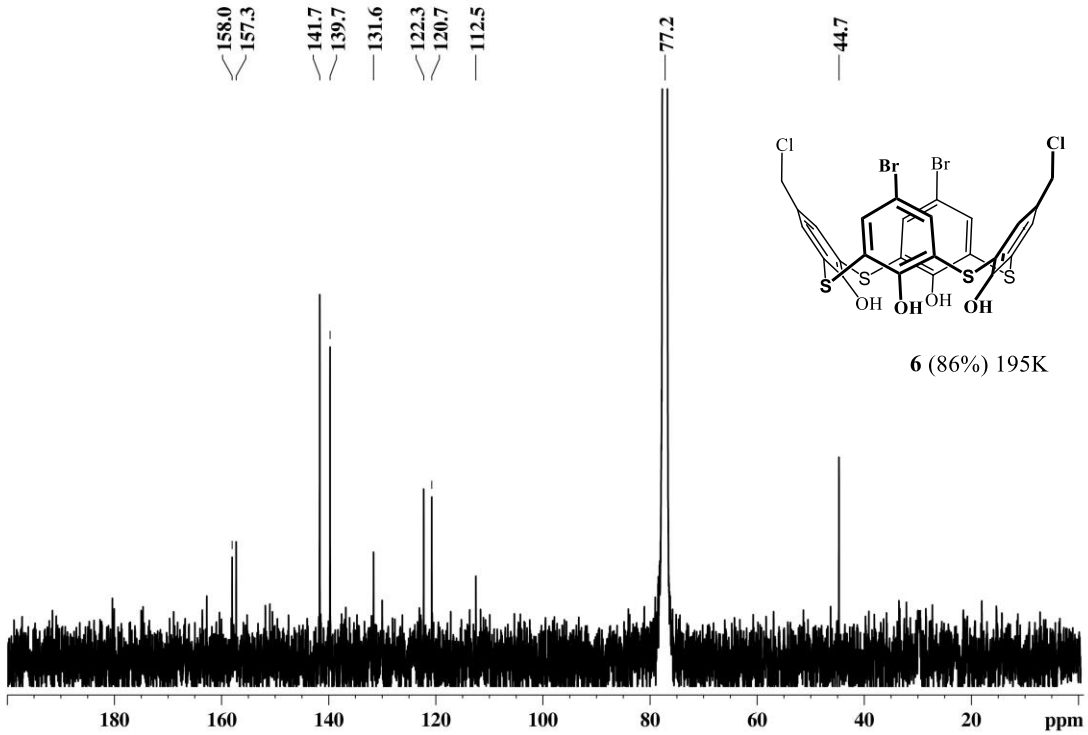


b)

Figure S7. ^{1}H NMR (a) and ^{13}C NMR (b) spectra ($CDCl_3$) of **5**.

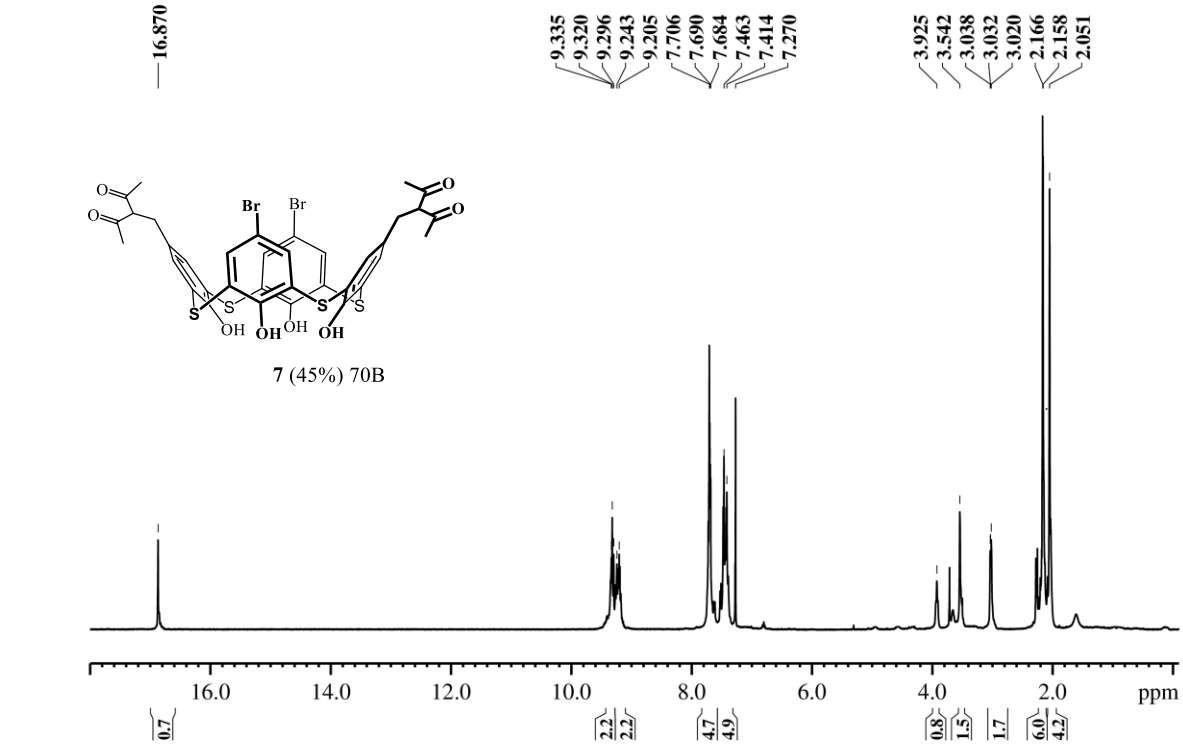


a)

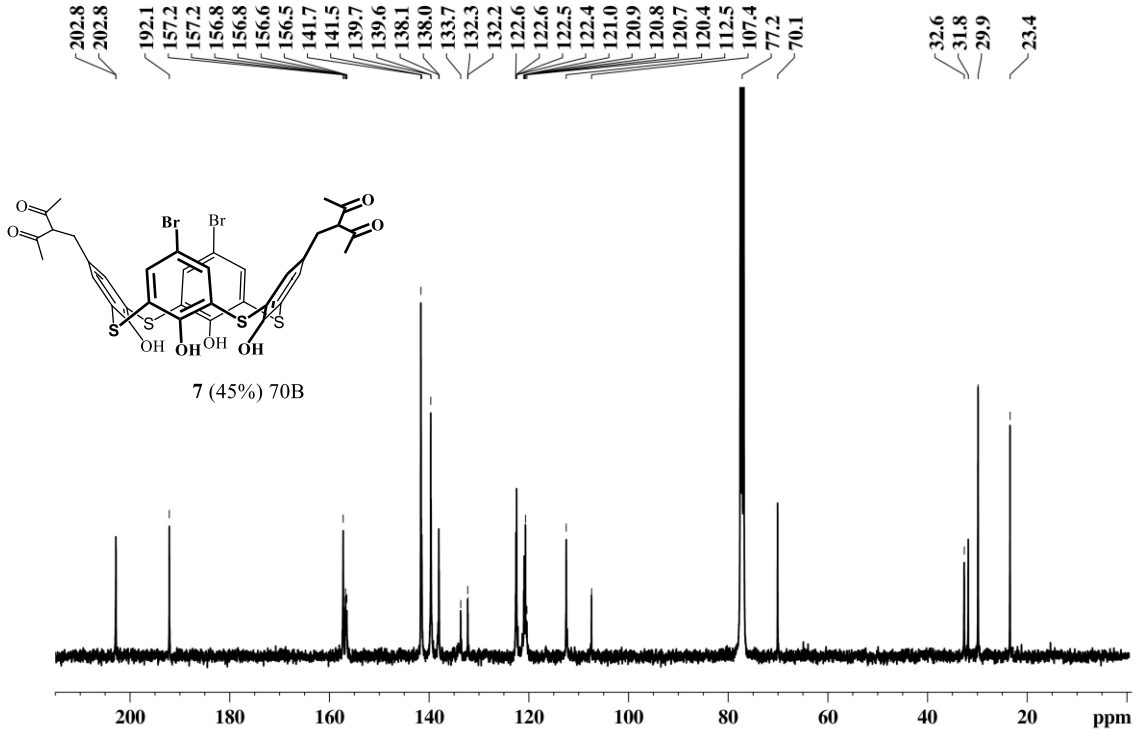


b)

Figure S8. ^{1}H NMR (a) and ^{13}C NMR (b) spectra ($CDCl_3$) of **6**.



a)



b)

Figure S9. ^{1}H NMR (a) and ^{13}C NMR (b) spectra ($CDCl_3$) of **7**.

Table S1. ^{1}H and ^{13}C chemical shifts[a] (ppm) and proton spin-spin coupling constants (Hz) observed for tetrathiacalix[4]arenes **4** in DMSO-d_6 and **5-7** in $CDCl_3$.

atom	compound							
	4		**5**		**6**		**7**[b]	
	^{1}H	^{13}C	^{1}H	^{13}C	^{1}H	^{13}C	^{1}H	^{13}C
1	7.561 t, ^{3}J=7.1	134.1					2.166 (2.051)	29.9 (23.4)
2	7.014 t, ^{3}J=7.1	128.6					(16.870 OH)	202.8 (192.1)
3	7.192 d, ^{3}J=7.1	130.1					3.925 t, ^{3}J=7.6	70.1 (107.4)
4		127.7			4.465	44.9	3.032 d, ^{3}J=7.6 (3.542)	32.6 (31.8)
5	7.592 t, ^{3}J=7.8	127.9	6.820 t, ^{3}J=7.7	122.2		131.6		132.3 (133.7)
5'		111.1		112.3		112.5		112.5
6	8.019 d, ^{3}J=7.8	135.1	7.640 d, ^{3}J=7.7	139.7	7.681	139.7	7.463	139.7 (138.1)
6'	7.406	137.0	7.720	141.5	7.747	141.7	7.706	141.7 (141.5)
7		129.4		120.5		120.7		120.7 (120.8)
7'		123.0		122.6		122.3		122.6 (122.5)
8		151.7		158.1		158.0		156.8 (156.5)
8'		156.5		157.3		157.3		157.3 (157.2)
9			9.271		9.323		9.320 m	
9’	8.572		9.348		9.282		9.320 m	
10		163.2						

[a] Numbering according to Figure S1

[b] The assignment for the enol form of bis-1,3-diketone is given in parentheses

4. **UV spectral data for compounds 1-2, 5** and **7 and their Tb^{3+} complexes**

Table S2. UV–spectral data for compounds **1-2, 5** and **7** after addition of TEA and Tb^{3+} to their DMF solutions (C_L=0.1 mM; $C_{TbNO3}{}^{3+}$ = 0.1 mM; C_{TEA}=0.8 mM).

Compound	λ_{max}(nm)/ (ε_{max}($M^{-1}cm^{-1}$))	Compound	λ_{max}(nm) (ε_{max}($M^{-1}cm^{-1}$))
1	293 (16800)	**5**	308 (18400)
	301 (17800)		342 (4800) sh
	332 (3500) sh		
1–TEA (1:8)	303 (21400)	**5**–TEA (1:8)	308 (18700)
	331 (6400) sh		340 (5600) sh
1–Tb^{3+}-TEA (1:1:8)	314 (19000)	**5**–Tb^{3+}-TEA (1:1:8)	323 (16500)
2	317 (19800)	**7**	310 (22500)
	350 (5100) sh		345 (4900) sh
2–TEA (1:8)	317 (19800)	**7**–TEA (1:8)	312 (24200)
	350 (5500) sh		345 (6800) sh
2–Tb^{3+}-TEA (1:1:8)	333 (18900)	**7**–Tb^{3+}-TEA (1:1:8)	325 (20300)

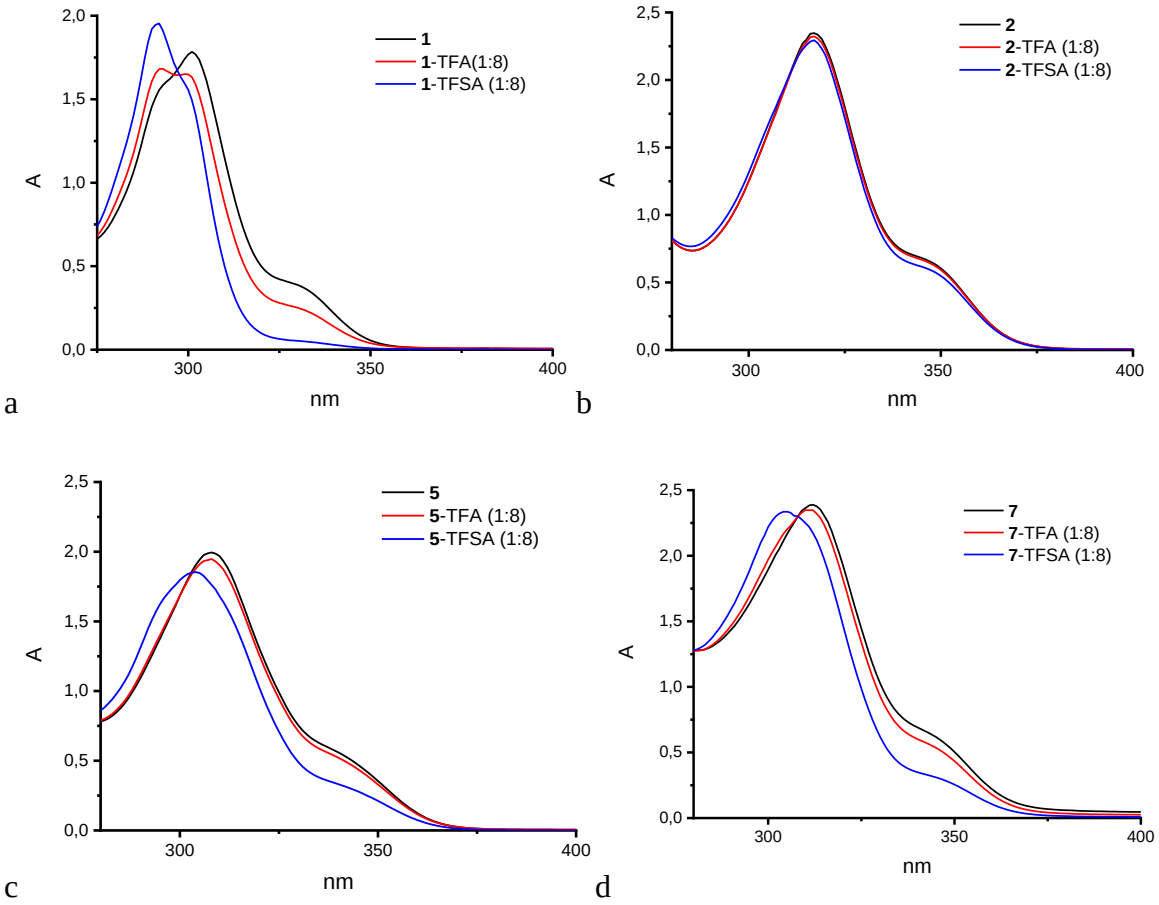
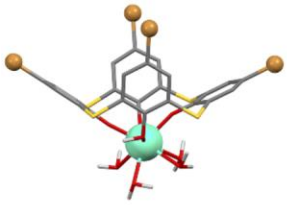
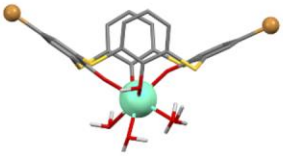


Fig. S10. UV-absorption spectra of L (L = **1** (a), **2** (b), **5** (c) and **7** (d)) (C_L=0.1 mM) in DMF; L with trifluoroacetic acid (TFA) (C_{TFA} = 0.8 mM) (L-TFA (1:8)); L with triflic acid (TFSA) (C_{TFSA}=0.8 mM) (L-TFSA (1:8).

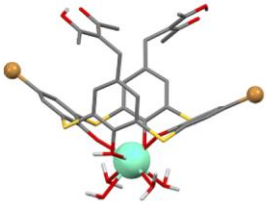
5. Optimized coordinates of atoms for ligands 2, 5, 7 and their Tb^{3+} complexes (I-X)



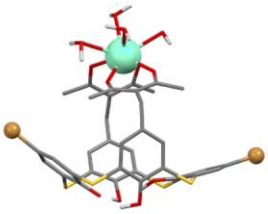
[Tb**2**$(H_2O)_4$]-(**I**)



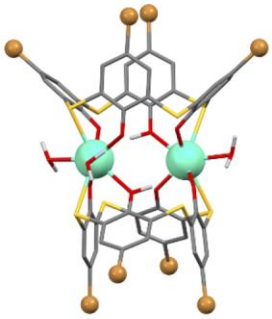
[Tb**5**$(H_2O)_4$]-(**II**)



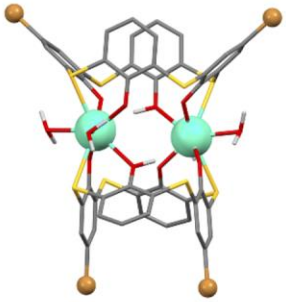
[Tb**7**$(H_2O)_4$]-(**III**)



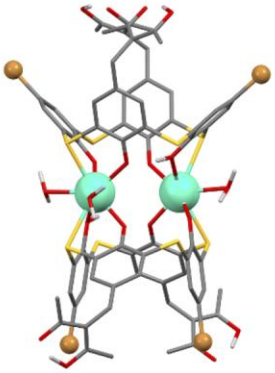
[Tb**7**$(H_2O)_4$]-(**IV**)



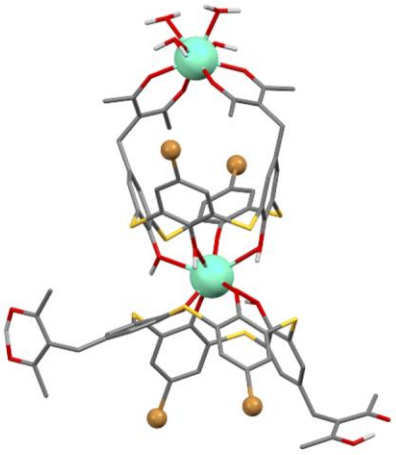
[Tb_2**2_2**$(H_2O)_4$]-(**V**)



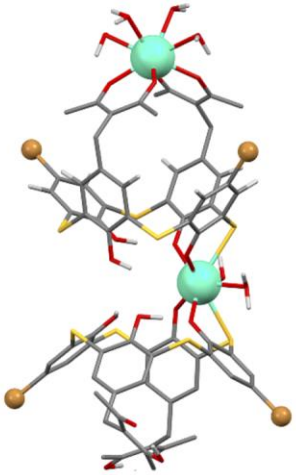
[Tb_2**5_2**$(H_2O)_4$]-(**VI**)



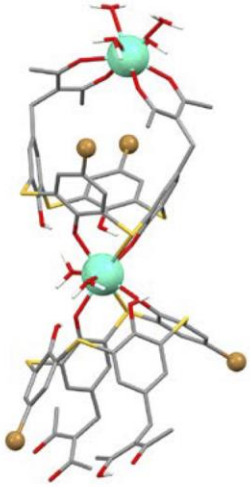
[Tb_2**7_2**$(H_2O)_4$]-(**VII**)



[Tb_2**7_2**$(H_2O)_4$]-(**VIII**)



[Tb_2**7_2**$(H_2O)_6$]-(**IX**)



[Tb_2**7_2**$(H_2O)_6$]-(**X**)

Cartesian coordinates (in Å) for [Tb**2**$(H_2O)_4$]-(**I**) optimized at the PBE/L1 level

```
   58
[Tb2(H2O)4]-(I)
 C     0.010214     3.106772    -2.411235
 C    -1.196916     2.416165    -2.476913
 C    -1.205458     1.034499    -2.698185
 C     0.010821     0.349520    -2.859832
 C     1.221519     1.073107    -2.816465
 C     1.224942     2.450413    -2.595075
 S    -2.800169     0.199499    -2.838958
 C    -3.425563     0.288414    -1.156902
 C    -2.717535    -0.404092    -0.133467
 C    -3.355101    -0.493973     1.137709
 C    -4.584820     0.124043     1.380296
 C    -5.221209     0.820642     0.352860
 C    -4.657335     0.904416    -0.918771
 S     2.745398     0.161370    -3.129010
 C     3.454528     0.001588    -1.481693
 C     4.653777     0.675687    -1.234341
 C     5.278163     0.526336     0.000116
 C     4.705185    -0.261187     0.996171
 C     3.505512    -0.936703     0.752926
 C     2.846169    -0.849620    -0.511994
 O     0.042959    -1.007540    -3.045301
 S    -2.689325    -1.598049     2.391650
 C    -1.030474    -0.962507     2.722138
 C    -0.901719     0.190753     3.497814
 C     0.369019     0.673192     3.801046
 C     1.510320     0.009522     3.359271
 C     1.383591    -1.144802     2.582451
 C     0.106556    -1.676527     2.241961
 O    -1.565183    -0.962064    -0.370045
 S     2.875092    -2.011944     2.049129
 O    -0.026882    -2.756614     1.495070
 O     1.753740    -1.515818    -0.781558
 H    -2.144439     2.944135    -2.359072
 H     2.168923     2.996288    -2.568187
 H    -5.044998     0.046927     2.367077
 H     2.503453     0.383936     3.613104
 H    -1.793045     0.705400     3.860506
 H     5.090401     1.309428    -2.007970
 H     5.184427    -0.358026     1.971923
 H    -5.170713     1.432852    -1.723946
 H     1.026272    -1.199757    -3.155913
Br    -6.910434     1.676032     0.695518
Br    -0.003099     5.001975    -2.101910
Br     6.935133     1.441813     0.343992
Br     0.548257     2.264593     4.869131
Tb    -0.143091    -2.513064    -0.746828
 O     1.146996    -4.532560     0.108734
 O     0.364151    -4.004595    -2.695268
 O    -2.067424    -2.983396    -2.506371
 O    -2.181894    -3.883990     0.094022
 H    -2.341148    -2.051262    -2.733597
 H    -2.693392    -3.303472    -1.820644
 H     0.552909    -4.943844    -2.510627
 H    -0.551712    -3.956489    -3.065343
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H	2.102057	-4.400744	-0.055279
H	0.999256	-4.036758	0.973503
H	-2.324190	-3.271460	0.880225
H	-1.940904	-4.737858	0.503893

Cartesian coordinates (in Å) for [Tb**5**(H_2O)$_4$]-(**II**) optimized at the PBE/L1 level

58
[Tb5(H2O)4]-(II)

C	-0.060187	4.232353	-0.800141
C	1.129206	3.753846	-0.252872
C	1.123403	2.859531	0.823361
C	-0.105740	2.442200	1.362646
C	-1.307440	2.950806	0.824061
C	-1.280313	3.841638	-0.249028
S	2.702473	2.332041	1.522518
C	3.370466	1.292973	0.217012
C	2.677328	0.094569	-0.117517
C	3.343904	-0.809824	-0.994175
C	4.589433	-0.499803	-1.547299
C	5.210714	0.704157	-1.215631
C	4.617862	1.603597	-0.331684
S	-2.847691	2.460158	1.623234
C	-3.521945	1.248253	0.473832
C	-4.706782	1.583967	-0.187409
C	-5.303224	0.653038	-1.032100
C	-4.717957	-0.592739	-1.246116
C	-3.532483	-0.932943	-0.587426
C	-2.902738	-0.027882	0.321921
O	-0.159124	1.541640	2.394773
S	2.690928	-2.469620	-1.229592
C	1.048424	-2.220161	-1.941107
C	0.942445	-1.869723	-3.287907
C	-0.309311	-1.713313	-3.883802
C	-1.458981	-1.931272	-3.124736
C	-1.371616	-2.282516	-1.775478
C	-0.108130	-2.446122	-1.137832
O	1.511030	-0.173534	0.394844
S	-2.884001	-2.591981	-0.837019
O	-0.003373	-2.762479	0.140825
O	-1.826038	-0.344275	0.992884
H	2.092272	4.073313	-0.657637
H	-2.223362	4.224014	-0.645444
H	5.073199	-1.206851	-2.223747
H	-2.448544	-1.828622	-3.577116
H	1.855976	-1.720070	-3.868804
H	-5.153560	2.567815	-0.035170
H	-5.175706	-1.312582	-1.926858
H	5.120244	2.533311	-0.059001
H	-1.147506	1.463411	2.577577
Br	6.922611	1.129009	-1.988861
H	-0.034198	4.928065	-1.641173
Br	-6.941023	1.105077	-1.938915
H	-0.387509	-1.439746	-4.937950
Tb	0.063016	-1.100227	1.663642
O	-1.230146	-3.194976	2.320183
O	-0.500396	-0.951042	4.101543

O	1.944621	-0.283672	3.347603
O	2.109183	-2.671035	1.985363
H	2.219985	0.569576	2.908586
H	2.578244	-0.972907	3.050793
H	-0.684747	-1.791146	4.562241
H	0.409700	-0.665707	4.364081
H	-2.185782	-2.986669	2.321864
H	-1.048704	-3.386134	1.346521
H	2.274709	-2.725242	0.992856
H	1.862244	-3.584410	2.229944

Cartesian coordinates (in Å) for [Tb**7**(H_2O)$_4$]-(**III**) optimized at the PBE/L1 level

90
[Tb7(H2O)4]-(III)

C	2.710542	-1.146636	0.489272
C	3.609966	-0.384182	-0.313495
C	4.772579	0.165056	0.237912
C	5.079127	-0.053935	1.580870
C	4.243594	-0.811508	2.397565
C	3.076280	-1.351749	1.850042
S	3.406299	-0.284209	-2.096441
C	1.776544	0.449689	-2.337966
C	1.623013	1.832037	-2.227059
C	0.391649	2.455876	-2.460488
C	-0.686286	1.648363	-2.840327
C	-0.553652	0.264145	-2.961505
C	0.689025	-0.388091	-2.722926
S	-1.984248	-0.716177	-3.485652
C	-3.047901	-0.617218	-2.037654
C	-4.216076	0.143832	-2.130059
C	-5.081295	0.222815	-1.040916
C	-4.783923	-0.430631	0.151955
C	-3.619585	-1.198128	0.243610
C	-2.716558	-1.342001	-0.852383
S	-3.350644	-2.116560	1.769482
C	-1.861281	-1.365854	2.461389
C	-1.893881	-0.149518	3.145296
C	-0.733130	0.379532	3.715213
C	0.453216	-0.357358	3.602835
C	0.510389	-1.575328	2.922250
C	-0.658191	-2.088883	2.335395
S	2.078073	-2.470048	2.842153
C	-0.727132	1.701555	4.480057
C	-1.966865	2.554673	4.363689
C	-2.969600	2.525663	5.338305
O	-4.032620	3.289453	5.246968
O	-0.644379	-3.261443	1.628407
Br	-6.691122	1.267452	-1.177404
O	-1.659239	-2.102587	-0.768920
C	0.204637	3.960012	-2.288418
C	1.414773	4.817338	-2.581869
C	1.798449	5.121752	-3.935237
O	2.801962	5.853360	-4.192380
O	0.810886	-1.695700	-2.836970
Br	6.683748	0.711981	2.322523
O	1.615437	-1.666153	0.007549
C	-2.162257	3.444871	3.250732

O	-3.189601	4.183500	3.166679
C	-1.139401	3.524178	2.140151
C	2.203443	5.356476	-1.562140
O	3.242431	6.115232	-1.829609
C	1.948518	5.136419	-0.094268
C	-2.926244	1.641736	6.555288
C	1.002282	4.574541	-5.096914
H	5.439573	0.754814	-0.393730
H	4.493302	-0.990668	3.444596
H	-1.659510	2.104546	-3.048745
H	-5.451454	-0.351758	1.011664
H	-4.440777	0.673271	-3.057662
H	1.374990	0.025345	4.052043
H	-2.838411	0.394192	3.227110
H	2.496067	2.437246	-1.967333
H	-0.131434	4.153930	-1.254599
H	-0.640139	4.274503	-2.926121
H	0.153129	2.278604	4.146606
H	-0.534199	1.480334	5.544180
H	0.904053	3.479802	-5.025672
H	1.505898	4.849953	-6.032641
H	-0.017581	4.995041	-5.097525
H	2.815334	5.502731	0.472168
H	1.783240	4.072549	0.132752
H	1.054726	5.694515	0.231402
H	-2.674296	0.603796	6.290886
H	-3.906884	1.669032	7.048904
H	-2.165433	2.001411	7.268318
H	-0.185639	3.927649	2.520128
H	-1.526380	4.188575	1.356428
H	-0.930251	2.527885	1.718443
H	3.250400	6.152503	-2.912733
H	-3.868319	3.835564	4.322582
H	-1.599722	-3.323615	1.315047
Tb	0.313414	-2.959636	-1.062799
O	-0.947979	-3.827541	-3.241679
O	1.687797	-4.538128	0.312731
O	2.132029	-3.857280	-2.513531
O	-0.985516	-5.182440	-0.953065
H	-1.827422	-5.161727	-0.459382
H	-1.249796	-5.025232	-1.896604
H	2.250885	-2.917454	-2.827355
H	2.924836	-4.084759	-1.990346
H	-0.219837	-3.908738	-3.889601
H	-1.305189	-2.900146	-3.389044
H	1.795370	-4.022981	1.163440
H	1.187088	-5.342009	0.553800

Cartesian coordinates (in Å) for [Tb**7**(H_2O)$_4$]-(**IV**) optimized at the PBE/L1 level

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   90
[Tb7(H2O)4]-(IV)
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C	4.163138	-3.357465	0.194817
C	3.402390	-3.935319	-0.823685
C	2.084288	-4.244716	-0.553360
C	1.409569	-3.955773	0.696123
C	2.266005	-3.374441	1.714502
C	3.611484	-3.093853	1.450232

S	1.060767	-5.022573	-1.842338
C	-0.080713	-3.721001	-2.320944
C	-1.437475	-3.806033	-1.939392
C	-2.315089	-2.810050	-2.434241
C	-1.806630	-1.692563	-3.099729
C	-0.443971	-1.566987	-3.413674
C	0.375423	-2.649291	-3.084146
S	1.736199	-3.142698	3.436631
C	0.648028	-1.729936	3.286196
C	1.055824	-0.459829	3.710275
C	0.200679	0.652472	3.713773
C	-1.134034	0.412915	3.379513
C	-1.615712	-0.858239	3.032458
C	-0.706660	-1.933559	2.875089
O	0.158382	-4.181359	0.839285
S	-4.097836	-2.870566	-2.086211
C	-4.352239	-1.682589	-0.782716
C	-5.474016	-0.848887	-0.905880
C	-5.842996	-0.025653	0.152554
C	-5.137501	-0.041165	1.350611
C	-4.034308	-0.893696	1.482768
C	-3.584078	-1.673539	0.401508
C	0.165637	-0.298507	-3.978357
C	0.482616	0.781290	-2.937807
C	-0.476679	1.803628	-2.666724
C	-1.867203	1.779095	-3.261162
O	-1.874047	-4.732902	-1.074827
S	-3.427995	-1.030631	3.153596
Br	-7.334753	1.179224	-0.063292
O	-2.415044	-2.324237	0.371418
C	0.657054	2.053233	4.092666
C	1.051195	2.849002	2.848491
C	2.364405	2.745778	2.310732
C	3.470560	2.050968	3.070158
O	-1.232875	-3.149463	2.543666
Br	6.007223	-2.882669	-0.149436
C	0.104768	3.728514	2.261391
C	-1.182850	4.109073	2.959207
C	1.683029	0.708930	-2.172822
C	2.719345	-0.361172	-2.384529
O	0.260747	4.297975	1.114389
Tb	1.478856	3.641406	-0.663257
O	2.167365	3.985898	-3.049962
O	2.752268	3.247380	1.181070
O	1.933650	1.512370	-1.190077
O	-0.249183	2.814661	-1.900532
O	4.013998	3.154814	-1.260612
O	-0.092936	5.464631	-1.483013
O	2.589361	5.876887	-0.543331
H	3.805314	-4.047231	-1.835657
H	4.238448	-2.663696	2.233503
H	-2.525310	-0.928967	-3.405711
H	-5.441858	0.582191	2.192177
H	-6.040184	-0.829110	-1.838986
H	2.084158	-0.359258	4.069778
H	-1.873383	1.210212	3.517234
H	1.425272	-2.660691	-3.384120
H	-0.499180	0.135145	-4.740335

H	1.089023	-0.564598	-4.518789
H	1.496527	1.996641	4.803793
H	-0.151024	2.563086	4.633902
H	2.478805	-1.227652	-1.741876
H	3.705835	0.009158	-2.066239
H	2.777720	-0.718829	-3.420212
H	-2.266040	2.803561	-3.288302
H	-2.519999	1.179511	-2.601914
H	-1.920279	1.340300	-4.265190
H	-1.960697	3.361798	2.726091
H	-1.519254	5.075000	2.555514
H	-1.093681	4.178531	4.050846
H	3.304789	1.999302	4.153355
H	4.414913	2.577081	2.864006
H	3.568546	1.018649	2.689137
H	2.681020	6.237445	0.359732
H	3.676335	2.223720	-1.178163
H	-0.600657	5.540297	-0.644650
H	1.844531	3.249507	-3.609880
H	3.132026	3.829671	-2.932963
H	-0.587624	4.765729	-1.980155
H	2.018097	6.505663	-1.031011
H	4.435782	3.327748	-0.394070
H	-0.783502	-3.594532	1.770295
H	-1.026849	-5.141061	-0.724702
H	-2.001077	-2.678693	1.230752

Cartesian coordinates (in Å) for [Tb_2**2**$_2$(H_2O)$_4$]-(**V**) optimized at the PBE/L1 level

104
[Tb222(H2O)4]-(V)

C	-3.466453	-1.201957	2.747005
C	-4.852444	-1.333696	2.842993
C	-4.796993	-3.078920	1.160317
C	-3.409075	-2.941512	1.051450
C	-2.737457	-1.998855	1.844758
S	-2.538153	-0.050148	3.776830
C	-3.332756	3.325357	1.597005
C	-4.309950	3.952066	2.371512
C	-4.708946	3.367326	3.573026
C	-3.196454	1.516514	3.194201
C	-2.701087	2.096129	1.984097
S	-2.815219	4.079328	0.044175
C	-3.158477	1.189835	-2.826268
C	-4.540629	1.136322	-3.021177
C	-5.384607	1.962322	-2.283406
C	-4.869902	2.863408	-1.356762
C	-3.488956	2.911718	-1.162675
C	-2.580225	2.093339	-1.891775
S	-2.071306	0.118926	-3.785087
C	-2.954316	-3.279839	-1.684149
C	-3.832179	-3.956683	-2.538147
C	-4.126616	-3.397068	-3.777434
C	-2.727794	-1.473667	-3.283491
C	-2.333244	-2.032778	-2.023759
S	-2.522512	-4.020097	-0.099016
C	-3.590635	-2.160041	-4.141797
C	-4.167569	2.149464	3.977435

C	-5.506046	-2.265522	2.040247
O	-1.273495	2.178677	-1.717670
O	-1.370662	-1.857868	1.761192
O	-1.734230	1.576112	1.285222
O	-1.448981	-1.480629	-1.240743
Tb	0.164658	-2.588585	-0.198435
Tb	-0.166790	2.704729	0.171120
C	3.161311	-3.340806	1.527092
C	4.043213	-4.029487	2.368874
C	3.660564	-2.367658	4.086519
C	2.793240	-1.667470	3.244004
C	2.467311	-2.155312	1.937623
S	2.847908	-3.995495	-0.127409
C	3.503596	-0.990374	-2.809342
C	4.893139	-0.993894	-2.938038
C	5.652504	-1.886322	-2.185616
C	3.650111	-2.785937	-1.201120
C	2.822641	-1.892766	-1.942200
S	2.496012	0.152441	-3.783783
C	3.142611	3.397885	-1.418029
C	4.076431	4.143029	-2.150037
C	4.505806	3.687096	-3.395015
C	4.052963	2.472323	-3.907329
C	3.130359	1.718529	-3.176235
C	2.633559	2.198835	-1.948013
S	2.608698	4.017168	0.188003
C	3.085090	1.022790	2.897954
C	4.467757	1.015052	3.090724
C	5.282898	1.901820	2.389776
C	3.352783	2.822442	1.309840
C	2.470011	1.942125	1.999555
S	2.049910	-0.136642	3.811935
C	4.735365	2.821638	1.502181
C	5.039258	-2.792753	-1.323477
C	4.265737	-3.549498	3.656029
O	1.653748	1.517396	-1.278948
O	1.571481	-1.586017	1.175317
O	1.511880	-1.895818	-1.848082
O	1.169298	1.988334	1.823641
H	-5.411972	-0.709981	3.541399
H	-5.314697	-3.818773	0.547900
H	-4.753983	4.890735	2.033529
H	-4.957243	0.439886	-3.750510
H	-5.531343	3.517561	-0.786193
H	-4.267494	-4.911172	-2.235709
H	-3.842133	-1.714174	-5.106100
H	-4.491428	1.684048	4.910207
H	4.541509	-4.933943	2.014188
H	3.861910	-1.976337	5.085642
H	5.382826	-0.297291	-3.620441
H	4.462008	5.075280	-1.733257
H	4.407837	2.103202	-4.870740
H	4.910744	0.304501	3.790449
H	5.371043	3.527623	0.965199
H	5.636584	-3.501865	-0.747553
O	0.033452	-4.094224	-2.174805
O	0.207226	-4.240594	1.709659
O	-0.279269	4.168473	2.150691

O	0.040751	4.377193	-1.702683
H	0.265412	3.475616	2.610660
H	-1.145459	4.191749	2.609339
H	-0.498950	3.695297	-2.198618
H	0.854571	4.528922	-2.221112
H	0.596420	-3.439141	-2.659107
H	-0.841050	-4.080575	-2.621178
H	-0.334485	-3.767467	2.376356
H	1.112608	-4.264713	2.097587
H	1.412528	0.730157	-1.856905
H	-1.149616	-1.008817	2.252308
Br	5.762122	4.730371	-4.400715
Br	7.185033	1.873927	2.674398
Br	5.442138	-4.505626	4.839198
Br	7.566381	-1.885641	-2.359836
Br	-7.286570	1.875718	-2.566340
Br	-5.298102	-4.325020	-4.987355
Br	-7.409950	-2.456025	2.172776
Br	-6.028634	4.236497	4.666215

Cartesian coordinates (in Å) for [Tb_2**5**$_2$(H_2O)$_4$]-(**VI**) optimized at the PBE/L1 level

104
[Tb252(H2O)4]-(VI)

C	3.622722	-0.446725	2.968252
C	4.999231	-0.298048	3.145348
C	4.788132	2.085743	2.850204
C	3.408456	1.956229	2.657574
C	2.821318	0.682408	2.714371
S	2.795966	-2.044685	3.081734
C	3.707310	-3.366644	-0.689163
C	4.747207	-4.263789	-0.441746
C	5.156864	-4.489642	0.871790
C	3.525468	-2.893663	1.675754
C	3.021673	-2.661898	0.356878
S	3.176566	-3.073377	-2.387059
C	3.272030	0.973266	-2.955903
C	4.642537	1.208732	-3.086703
C	5.569673	0.169881	-2.999333
C	5.116046	-1.131776	-2.792382
C	3.749757	-1.378436	-2.656371
C	2.775433	-0.343179	-2.745823
S	2.096685	2.335752	-3.076048
C	2.852333	3.830057	0.661375
C	3.671996	4.932648	0.396331
C	3.965946	5.245982	-0.926659
C	2.681596	3.337385	-1.706576
C	2.291069	3.003201	-0.367571
S	2.422010	3.444548	2.368963
C	3.485774	4.449674	-1.968309
C	4.560412	-3.801135	1.925188
C	5.584924	0.965235	3.077574
O	1.481240	-0.597341	-2.654956
O	1.463551	0.529048	2.543275
O	2.002460	-1.893436	0.106688
O	1.458666	2.041418	-0.083968
Tb	-0.175954	2.195058	1.408631
Tb	0.467953	-2.224965	-1.478458

C	-3.147700	1.570401	3.223774
C	-4.033422	1.548867	4.307757
C	-3.505374	-0.768902	4.676735
C	-2.630307	-0.772905	3.587558
C	-2.379170	0.421750	2.838953
S	-2.924267	3.103294	2.293862
C	-3.500394	2.264009	-1.659234
C	-4.891384	2.239581	-1.767206
C	-5.673204	2.448886	-0.634263
C	-3.694452	2.729128	0.703616
C	-2.844270	2.520396	-0.421006
S	-2.460788	2.000667	-3.116138
C	-2.847733	-2.048277	-3.192974
C	-3.764372	-2.254462	-4.232668
C	-4.272236	-1.179485	-4.962094
C	-3.895535	0.121222	-4.625361
C	-2.991465	0.350364	-3.584184
C	-2.426967	-0.740026	-2.891450
S	-2.222415	-3.466882	-2.274295
C	-2.778993	-2.728509	1.687363
C	-4.154526	-2.917358	1.833510
C	-4.940058	-3.256502	0.733840
C	-2.996239	-3.234771	-0.665073
C	-2.142836	-2.892043	0.422799
S	-1.780070	-2.282340	3.120262
C	-4.371081	-3.429962	-0.522901
C	-5.085057	2.704425	0.602388
C	-4.198086	0.384653	5.056491
O	-1.464149	-0.534651	-1.940638
O	-1.482730	0.484427	1.888816
O	-1.533477	2.563866	-0.336602
O	-0.846890	-2.745436	0.265895
H	5.607954	-1.184271	3.336774
H	5.231100	3.083535	2.812052
H	5.230403	-4.779812	-1.274020
H	4.984997	2.232370	-3.256342
H	5.820709	-1.964940	-2.730714
H	4.061701	5.537762	1.217262
H	3.734583	4.688709	-3.004045
H	4.889759	-3.969204	2.952202
H	-4.587351	2.457836	4.557593
H	-3.642350	-1.701436	5.230827
H	-5.363136	2.050274	-2.732706
H	-4.075978	-3.277706	-4.456571
H	-4.299606	0.979080	-5.167614
H	-4.614132	-2.789439	2.814839
H	-4.983601	-3.709130	-1.381741
H	-5.701657	2.881005	1.485449
O	-0.187430	4.593079	0.730614
O	-0.246728	2.340013	3.928864
O	0.730971	-4.575418	-0.772794
O	0.279950	-2.425710	-3.987002
H	0.158573	-4.324053	0.001480
H	1.612473	-4.798414	-0.406157
H	0.772085	-1.553398	-3.951068
H	-0.560866	-2.254897	-4.454948
H	-0.735656	4.310191	-0.045408
H	0.672257	4.888703	0.359494

H	0.338200	1.584792	4.152584
H	-1.142998	2.056253	4.226902
H	-1.286554	0.455980	-1.931650
H	1.309560	-0.457258	2.422051
H	-4.979080	-1.354547	-5.775702
Br	-6.834522	-3.515843	0.961304
H	-4.878102	0.367221	5.910414
Br	-7.590706	2.410324	-0.784799
H	6.637165	0.372148	-3.107216
Br	5.060671	6.779522	-1.321700
H	6.661445	1.079211	3.219256
Br	6.568197	-5.746834	1.229383

Cartesian coordinates (in Å) for [Tb_2**7**$_2$(H_2O)$_4$]-(**VII**) optimized at the PBE/L1 level

168
[Tb272(H2O)4]-(VII)

C	-3.575808	-0.037057	-3.108261
C	-4.947254	0.135309	-3.298849
C	-4.768621	2.409728	-2.473523
C	-3.395016	2.238124	-2.269380
C	-2.796479	1.008131	-2.579369
S	-2.723740	-1.560458	-3.557524
C	-3.445123	-3.611550	-0.096887
C	-4.465618	-4.479837	-0.489907
C	-4.948859	-4.489087	-1.802546
C	-3.371424	-2.688600	-2.318673
C	-2.824189	-2.683654	-0.996449
S	-2.881077	-3.625107	1.614643
C	-3.264224	0.176449	3.059399
C	-4.643214	0.276060	3.259116
C	-5.476840	-0.791080	2.936191
C	-4.952489	-1.980831	2.440198
C	-3.575539	-2.075757	2.237711
C	-2.678028	-1.009905	2.535401
S	-2.201011	1.561590	3.501202
C	-2.913955	3.685534	0.080506
C	-3.781133	4.691927	0.525463
C	-4.147887	4.773025	1.868596
C	-2.791165	2.768748	2.312673
C	-2.367586	2.680814	0.944833
S	-2.427755	3.638014	-1.653394
C	-3.640286	3.791602	2.736289
C	-4.388802	-3.568497	-2.696369
C	-5.532489	1.354874	-2.966140
Br	-7.378258	-0.631340	3.208461
Br	-7.419028	1.599527	-3.225813
C	-6.030923	-5.458545	-2.267944
C	-5.062580	5.871574	2.402228
C	-5.954033	6.546223	1.385291
O	-1.378538	-1.127530	2.354991
O	-1.446812	0.814963	-2.394882
O	-1.833700	-1.918957	-0.630524
O	-1.526135	1.784903	0.506838
C	-6.942765	-6.003913	-1.193570
C	-7.144713	5.938416	0.962524
C	-5.637934	7.823675	0.815533
C	-8.032467	-5.220131	-0.672482

C	-6.780044	-7.291313	-0.673492
O	-8.814549	-5.681182	0.212651
O	-7.592763	-7.765708	0.242090
C	-8.277116	-3.816092	-1.174364
C	-5.693505	-8.241283	-1.102049
O	-7.933131	6.517826	0.091455
C	-7.607677	4.601178	1.465872
O	-6.407630	8.381660	-0.028301
C	-4.372792	8.562078	1.199170
Tb	0.143922	2.160423	-0.909033
Tb	-0.253923	-2.416656	0.887311
C	3.201207	2.163022	-2.673040
C	4.243894	2.440737	-3.566196
C	3.975163	0.236821	-4.524897
C	2.943459	-0.052012	-3.630908
C	2.487267	0.919079	-2.679331
S	2.695507	3.467122	-1.525129
C	3.440618	2.175491	2.281769
C	4.718409	2.689009	2.502127
C	5.408128	3.407986	1.517999
C	3.486976	3.076187	0.047572
C	2.780189	2.319306	1.025179
S	2.544921	1.409013	3.642220
C	2.988493	-2.533102	2.597194
C	3.881417	-2.984948	3.576754
C	4.376051	-2.095693	4.525899
C	3.996301	-0.757851	4.503135
C	3.095213	-0.297428	3.534886
C	2.566470	-1.182707	2.569199
S	2.350771	-3.772742	1.448025
C	3.042018	-2.459670	-2.330022
C	4.384081	-2.799836	-2.502368
C	5.136781	-3.441285	-1.508746
C	3.159529	-3.361347	-0.101571
C	2.359259	-2.752070	-1.111034
S	2.156400	-1.666606	-3.689705
C	4.494731	-3.716935	-0.300286
C	4.753805	3.609492	0.300154
C	4.615451	1.477623	-4.496414
Br	5.600149	-2.719274	5.866101
Br	6.030349	1.850494	-5.745205
C	6.804562	3.962103	1.770852
C	6.574452	-3.882519	-1.754671
C	7.502295	-2.811863	-2.289211
O	1.641246	-0.799812	1.643679
O	1.466317	0.701635	-1.897805
O	1.589433	1.787323	0.812442
O	1.081774	-2.509017	-0.928880
C	7.800273	2.931778	2.261226
C	8.051935	-1.809224	-1.411175
C	7.884512	-2.763767	-3.632041
C	8.346921	1.949342	1.358688
C	8.227433	2.886130	3.590748
O	9.138859	1.046954	1.773706
O	9.065925	1.963729	4.006383
C	8.009480	1.981568	-0.110544
C	7.816042	3.874590	4.651795
O	8.820198	-0.898803	-1.850312

C	7.740710	-1.828655	0.066038
O	8.690486	-1.826618	-4.081956
C	7.465682	-3.764053	-4.677289
H	-5.546119	-0.679590	-3.707412
H	-5.231328	3.370381	-2.241552
H	-4.903859	-5.153313	0.252772
H	-5.061560	1.196534	3.669331
H	-5.603690	-2.826324	2.211108
H	-4.177893	5.413675	-0.194418
H	-3.922224	3.810365	3.794406
H	-4.749558	-3.528426	-3.729420
H	-5.545541	-6.301379	-2.790730
H	-6.631172	-4.951072	-3.043770
H	-4.440840	6.635511	2.901057
H	-5.678412	5.436169	3.208939
H	-7.367859	-3.200475	-1.088541
H	-9.090706	-3.367773	-0.589710
H	-8.563851	-3.832376	-2.239508
H	-5.660778	-9.082092	-0.396035
H	-4.710138	-7.748631	-1.131358
H	-5.901074	-8.639477	-2.109483
H	-6.812701	3.845331	1.373158
H	-8.490465	4.285482	0.894612
H	-7.879026	4.664290	2.533240
H	-4.417370	8.889486	2.251352
H	-4.277372	9.446626	0.555727
H	-3.481812	7.923901	1.087958
H	4.746939	3.409046	-3.532419
H	4.277209	-0.521465	-5.249478
H	5.182765	2.516364	3.476995
H	4.181243	-4.034290	3.582057
H	4.383197	-0.054116	5.241217
H	4.858013	-2.548422	-3.455415
H	5.036274	-4.224247	0.504606
H	5.240156	4.193604	-0.487687
H	6.738124	4.784388	2.502746
H	7.164053	4.427998	0.837042
H	6.567789	-4.737299	-2.451893
H	6.973729	-4.286862	-0.808603
H	6.921930	1.886391	-0.262189
H	8.527394	1.164150	-0.630604
H	8.311822	2.947362	-0.549948
H	8.165579	3.508488	5.626499
H	6.726331	4.019379	4.686239
H	8.276521	4.858465	4.461705
H	6.659309	-1.692604	0.232863
H	8.303958	-1.033215	0.572552
H	8.012486	-2.802641	0.505699
H	6.417768	-4.074907	-4.568837
H	8.094914	-4.668069	-4.609360
H	7.616460	-3.318297	-5.670136
H	8.899239	-1.235398	-3.206706
H	9.252923	1.377256	3.112608
H	-8.289255	-6.949368	0.404170
H	-7.416125	7.454930	-0.125721
O	0.104067	4.337126	0.311023
O	0.197319	2.903061	-3.357011
O	-0.423729	-4.588692	-0.296482

O	-0.060793	-3.084483	3.324560
H	0.112370	-4.139619	-1.004159
H	-1.315420	-4.734112	-0.679982
H	-0.589706	-2.243611	3.450738
H	0.766261	-2.976620	3.833838
H	0.656416	4.201118	1.108585
H	-0.813200	4.466354	0.652183
H	-0.325595	2.155046	-3.718234
H	1.101968	2.762654	-3.716616
H	1.576199	0.219107	1.538715
H	-1.297866	-0.177960	-2.490865

Cartesian coordinates (in Å) for $[Tb_2\mathbf{7}_2(H_2O)_4]$-(**VIII**) optimized at the PBE/L1 level

168
[Tb272(H2O)4]-(VIII)

C	-3.602073	0.398589	2.825144
C	-4.798548	0.417842	3.562616
C	-5.343806	-1.783136	2.742185
C	-4.169292	-1.814078	1.990280
C	-3.242810	-0.720072	1.986549
S	-2.407196	1.705520	3.175265
C	-2.998585	3.963448	-0.181286
C	-2.648640	5.232588	0.297900
C	-2.386377	5.444664	1.655741
C	-2.766397	3.072025	2.070524
C	-3.106103	2.900087	0.722402
S	-2.948212	3.707601	-1.955484
C	-5.328589	0.640195	-3.247798
C	-6.555457	1.285522	-3.418316
C	-6.689967	2.623217	-3.059903
C	-5.600619	3.337726	-2.571284
C	-4.369954	2.700525	-2.395339
C	-4.185847	1.314298	-2.705547
S	-5.175706	-1.055712	-3.851878
C	-4.967837	-3.082926	-0.315606
C	-6.205308	-3.739990	-0.284346
C	-7.153558	-3.580987	-1.296837
C	-5.612696	-2.064170	-2.422010
C	-4.645425	-2.259261	-1.407722
S	-3.814243	-3.310053	1.047790
C	-6.838794	-2.723627	-2.360969
C	-2.441825	4.355245	2.531032
C	-5.667479	-0.661047	3.501853
Br	-8.389197	3.505695	-3.284460
Br	-7.309379	-0.631266	4.506921
C	-2.052404	6.831138	2.197023
C	-8.516327	-4.270261	-1.262930
C	-8.754173	-5.248050	-0.137473
O	-3.053153	0.688196	-2.500610
O	-2.163949	-0.722013	1.229730
O	-3.439904	1.650327	0.232436
O	-3.437263	-1.657031	-1.499478
C	-1.332069	7.761137	1.247257
C	-9.339921	-4.843317	1.066778
C	-8.392734	-6.633954	-0.255308
C	-1.990299	8.852460	0.593209
C	0.031748	7.584272	0.970396

O	-1.359369	9.633093	-0.189848
O	0.672152	8.391656	0.162231
C	-3.464769	9.124785	0.803788
C	0.848303	6.472715	1.562774
O	-9.571921	-5.699265	2.034583
C	-9.746782	-3.425065	1.358162
O	-8.620977	-7.460573	0.680528
C	-7.719998	-7.150787	-1.507179
C	1.115619	-1.407662	3.696482
C	1.837710	-1.357944	4.895610
C	2.498425	0.923493	4.382949
C	1.745194	0.891916	3.201390
C	1.048637	-0.286092	2.836884
S	0.256839	-2.935705	3.261203
C	1.609001	-3.777035	-0.509919
C	2.960096	-4.031262	-0.267357
C	3.500997	-4.028405	1.027603
C	1.290759	-3.432859	1.868753
C	0.737246	-3.490039	0.570491
S	0.944605	-3.958025	-2.177669
C	0.994881	-0.038864	-3.427703
C	1.863965	-0.099541	-4.517937
C	2.479715	-1.310985	-4.822248
C	2.236729	-2.450465	-4.059357
C	1.345753	-2.401446	-2.981036
C	0.674202	-1.185587	-2.637671
S	0.209254	1.521550	-2.984946
C	1.916554	2.305960	0.642693
C	3.221650	2.642759	0.266724
C	3.618803	2.733712	-1.073980
C	1.368709	2.049137	-1.701617
C	0.919075	2.026814	-0.346797
S	1.477299	2.472465	2.381895
C	2.656929	2.440839	-2.047343
C	2.635014	-3.737597	2.083368
C	2.524446	-0.191444	5.218084
Br	3.705023	-1.407864	-6.315521
Br	3.563161	-0.127258	6.844544
C	4.951795	-4.402340	1.302846
C	5.019959	3.176458	-1.473540
C	6.124884	2.156173	-1.209400
O	-0.190091	-1.112852	-1.663759
O	0.376082	-0.306148	1.680693
O	-0.562607	-3.303113	0.317153
O	-0.328332	1.773154	-0.062134
C	6.008722	-3.383264	0.882490
C	6.273351	1.053817	-2.092372
C	7.024448	2.353235	-0.131914
C	6.217700	-2.233278	1.688011
C	6.814723	-3.635292	-0.256793
O	7.085766	-1.312116	1.424723
O	7.704443	-2.820182	-0.713309
C	5.420065	-2.013656	2.947329
C	6.696681	-4.940757	-1.021684
O	7.131690	0.101418	-1.924232
C	5.422839	0.928144	-3.327409
O	7.922831	1.501128	0.232827
C	7.007866	3.639901	0.672442

Tb	8.442302	-0.689591	-0.268898
H	-5.018745	1.281046	4.192480
H	-6.007756	-2.649084	2.726288
H	-2.554000	6.056779	-0.413641
H	-7.397533	0.734799	-3.840254
H	-5.692742	4.398928	-2.334513
H	-6.425443	-4.391823	0.565048
H	-7.559240	-2.559800	-3.168295
H	-2.192144	4.487978	3.588149
H	-1.457807	6.698297	3.118607
H	-2.990304	7.309241	2.527081
H	-8.664980	-4.780958	-2.230354
H	-9.293160	-3.486003	-1.234318
H	-4.073269	8.229081	0.602818
H	-3.766934	9.936236	0.128673
H	-3.661135	9.433181	1.844145
H	1.879108	6.543646	1.192201
H	0.425531	5.491347	1.293598
H	0.850658	6.530494	2.663780
H	-8.949782	-2.714656	1.092130
H	-9.980821	-3.332395	2.427109
H	-10.644674	-3.153592	0.777529
H	-8.410388	-7.103239	-2.366093
H	-7.426132	-8.195671	-1.342850
H	-6.835200	-6.546090	-1.761323
H	1.868810	-2.230903	5.549163
H	3.032646	1.835710	4.654203
H	3.587689	-4.264627	-1.131978
H	2.049367	0.792330	-5.119312
H	2.723459	-3.396540	-4.302407
H	3.930835	2.868477	1.068675
H	2.911645	2.516046	-3.108495
H	3.001443	-3.746513	3.113473
H	5.163176	-5.362327	0.809746
H	5.048142	-4.607245	2.382817
H	5.257601	4.112649	-0.948065
H	5.002647	3.442129	-2.543979
H	4.376240	-1.763370	2.692158
H	5.849921	-1.176969	3.513970
H	5.387576	-2.910931	3.584526
H	7.437752	-4.944856	-1.832818
H	5.694178	-5.063160	-1.460294
H	6.877278	-5.812257	-0.371366
H	4.404976	0.606964	-3.045415
H	5.846946	0.166526	-3.995404
H	5.320451	1.880601	-3.868663
H	7.051035	4.532882	0.029547
H	7.872905	3.644358	1.350145
H	6.089870	3.716058	1.277436
H	-0.108483	9.099583	-0.146766
H	-9.209438	-6.638529	1.626558
O	9.276852	0.084289	2.054802
O	9.133754	-1.542099	-2.585557
O	10.490033	0.486642	-1.111612
O	10.426629	-1.982778	0.557333
H	10.369994	1.411571	-1.401157
H	8.443257	-0.317491	2.407307
H	8.350819	-1.055690	-2.946267

H	10.289071	-2.902626	0.854004
H	10.614339	-1.458629	1.367543
H	8.762643	-2.432501	-2.374877
H	10.700016	-0.027117	-1.920801
H	8.998656	1.006087	1.834277
Tb	-1.642559	0.238957	-0.815896
H	-1.023697	-2.998444	1.135047
H	-0.562185	-0.661809	1.772824
H	-3.462553	-1.076796	-2.330733
H	-3.811661	1.129217	0.993261

Cartesian coordinates (in Å) for $[Tb_2\mathbf{7}_2(H_2O)_6]$-(**IX**) optimized at the PBE/L1 level

174
[Tb272(H2O)6]-(IX)

C	3.635473	5.010974	1.028467
C	2.981870	4.381391	2.085768
C	2.038218	3.383758	1.825204
C	1.729174	3.004102	0.488735
C	2.408028	3.674262	-0.561162
C	3.356601	4.668147	-0.289602
S	1.135937	2.662743	3.200051
C	1.835424	1.001400	3.198979
C	1.047293	-0.111762	2.821165
C	1.650820	-1.391773	2.869504
C	2.972638	-1.545101	3.290991
C	3.761431	-0.445790	3.648282
C	3.154314	0.816082	3.610799
S	1.937382	3.391559	-2.272293
C	2.643226	1.776615	-2.646101
C	3.941736	1.702968	-3.147465
C	4.512315	0.500571	-3.587902
C	3.693997	-0.634088	-3.569592
C	2.397071	-0.592071	-3.057983
C	1.821646	0.606872	-2.533395
O	0.821029	2.054346	0.302424
S	0.655170	-2.821781	2.398726
C	1.427870	-3.225886	0.820562
C	2.443855	-4.183267	0.819627
C	3.113485	-4.500466	-0.361380
C	2.784905	-3.863152	-1.552477
C	1.764156	-2.909576	-1.560058
C	1.002003	-2.573785	-0.388422
C	5.196923	-0.613948	4.128244
C	6.287996	-0.509135	3.059071
C	6.769664	-1.692154	2.424998
C	6.204708	-3.054917	2.758614
O	-0.221879	0.079147	2.459034
S	1.384531	-2.081006	-3.120538
Tb	-1.141085	-0.821640	-2.122250
O	-0.811186	0.069270	-4.470200
Br	4.518267	-5.828085	-0.341281
O	-0.003230	-1.757407	-0.425069
C	5.953361	0.436834	-4.069546
C	6.963562	0.207504	-2.944565
C	7.591403	1.318326	-2.309323
C	7.437601	2.730779	-2.832116
O	0.626234	0.648312	-2.013633

Br	4.959352	6.370353	1.401358
S	-3.426411	1.380088	3.617633
C	-4.400152	-0.096093	3.243061
C	-5.577338	-0.333135	3.955604
C	-6.310272	-1.518101	3.810219
C	-5.802656	-2.493772	2.949284
C	-4.621788	-2.288136	2.228288
C	-3.910357	-1.074362	2.344338
C	-7.623714	-1.700653	4.565456
C	-8.086151	-3.123691	4.773375
C	-9.055787	-3.708563	3.954222
C	-9.706869	-3.005937	2.793297
S	-3.910741	-3.656691	1.296139
C	-4.514836	-3.396994	-0.376865
C	-5.502762	-4.271153	-0.841957
C	-5.922667	-4.221538	-2.169251
C	-5.375273	-3.291627	-3.046352
C	-4.392901	-2.408566	-2.585176
C	-3.913563	-2.421620	-1.235406
Br	-7.272541	-5.445052	-2.792803
S	-3.697673	-1.219923	-3.741989
C	-4.430020	0.321857	-3.148165
C	-5.800734	0.538106	-3.277217
C	-6.382712	1.724961	-2.818848
C	-5.534549	2.692921	-2.271115
C	-4.159383	2.494130	-2.136679
C	-3.550773	1.285579	-2.578638
C	-7.891719	1.927233	-2.887232
C	-8.361826	3.347307	-3.115817
C	-8.817417	4.175036	-2.085296
C	-8.877103	3.807949	-0.630070
S	-3.153126	3.791164	-1.391534
C	-3.812175	3.723701	0.277662
C	-4.630626	4.754870	0.744283
C	-5.127132	4.711079	2.046246
C	-4.819760	3.654063	2.895916
C	-3.991107	2.620602	2.441236
C	-3.463642	2.641011	1.126456
O	-2.655302	1.694699	0.647139
O	-2.254329	1.062361	-2.487695
O	-2.954351	-1.612994	-0.843204
O	-2.782290	-0.838789	1.640212
Br	-6.278352	6.130294	2.669575
C	-7.547257	-3.935078	5.831862
C	-6.482088	-3.383524	6.751403
C	-8.339075	3.909807	-4.445056
C	-7.834499	3.088306	-5.610332
O	-7.945761	-5.123657	6.026269
O	-9.467671	-4.940171	4.155364
O	-8.731942	5.090079	-4.679723
O	-9.226983	5.403865	-2.327669
O	-1.379418	-3.273826	-2.702433
C	7.274371	-1.111472	-2.535457
C	6.769120	-2.331307	-3.269572
C	6.834976	0.752272	2.722047
C	6.423135	2.032493	3.407815
O	8.011653	-1.393290	-1.509622
Tb	8.915400	-0.300499	0.284189

O	10.677833	-0.534772	2.060571
O	8.335480	1.230958	-1.264416
O	7.718333	0.928610	1.788758
O	7.694426	-1.712635	1.531145
O	9.979270	1.926835	1.106207
O	9.853153	-2.672295	-0.260645
O	11.130474	-0.351149	-0.906415
H	-4.876015	5.583947	0.078515
H	-5.201834	3.624975	3.917153
H	-6.424356	-0.237948	-3.732946
H	-5.927117	-5.002463	-0.152042
H	-5.701519	-3.240063	-4.086775
H	-5.919986	0.440060	4.650190
H	-6.316021	-3.453752	2.849793
H	-5.954127	3.644669	-1.935049
H	-8.333185	1.544428	-1.951310
H	-8.292573	1.269715	-3.678363
H	-8.409139	-1.140574	4.028440
H	-7.529215	-1.192694	5.541184
H	-6.825101	2.696831	-5.407397
H	-7.822544	3.720796	-6.507539
H	-8.492190	2.220604	-5.787323
H	-9.858289	4.103097	-0.226977
H	-8.114128	4.381871	-0.077105
H	-8.707203	2.741778	-0.443141
H	-5.640393	-2.966496	6.176549
H	-6.129887	-4.189583	7.408092
H	-6.892955	-2.568172	7.370593
H	-10.386648	-2.214115	3.149825
H	-10.291641	-3.737177	2.219404
H	-8.959179	-2.535478	2.137178
H	3.187907	4.661652	3.120099
H	3.851126	5.175302	-1.119390
H	3.373727	-2.559078	3.360376
H	3.305971	-4.105963	-2.480706
H	2.701484	-4.684083	1.754759
H	4.507043	2.636097	-3.218470
H	4.057415	-1.582703	-3.974113
H	3.704420	1.702128	3.934271
H	5.281766	-1.586575	4.635492
H	5.389179	0.132989	4.914323
H	6.191909	1.370146	-4.600267
H	6.043250	-0.358412	-4.825522
H	5.641041	2.525901	2.803274
H	7.286451	2.714474	3.441887
H	6.029588	1.892802	4.421497
H	6.900139	-3.824913	2.397852
H	5.247908	-3.187700	2.224408
H	6.011086	-3.202621	3.830092
H	5.850668	-2.688576	-2.771387
H	7.519440	-3.131795	-3.184918
H	6.538644	-2.157016	-4.327542
H	7.287234	2.796783	-3.917172
H	8.331363	3.304989	-2.548118
H	6.570619	3.204063	-2.338764
H	-9.097404	5.510906	-3.384760
H	-8.888975	-5.257826	5.014534
H	11.131158	-0.107794	-1.851867

H	9.073753	2.038999	1.516323
H	9.085218	-2.674499	-0.899944
H	10.380563	-0.739655	2.967775
H	10.947221	0.412657	2.074685
H	9.612942	-3.303855	0.444683
H	11.244703	-1.329295	-0.880719
H	10.026230	2.579312	0.380882
H	-2.319742	-3.543140	-2.591384
H	0.093011	0.417591	-4.603285
H	-0.888041	-3.780103	-2.022931
H	-1.325532	0.834060	-4.089986
H	0.708239	1.797392	-0.663354
H	-0.610410	-0.785389	2.171454
H	-2.822427	-1.322599	0.734896
H	-2.552095	0.958771	1.311083

Cartesian coordinates (in Å) for $[Tb_2\mathbf{7}_2(H_2O)_6]$-(**X**) optimized at the PBE/L1 level

174
[Tb272(H2O)6]-(X)

C	-4.977405	5.087591	0.046688
C	-4.502893	4.879737	-1.246736
C	-3.408882	4.034241	-1.453048
C	-2.760021	3.408296	-0.356571
C	-3.269671	3.637399	0.946284
C	-4.377489	4.470465	1.140721
S	-2.774583	3.786203	-3.121432
C	-3.462163	2.148309	-3.448215
C	-2.651947	0.992418	-3.461505
C	-3.269387	-0.249407	-3.759927
C	-4.650583	-0.333327	-3.934175
C	-5.467678	0.804177	-3.871159
C	-4.836291	2.035985	-3.679284
S	-2.392804	3.025506	2.391900
C	-2.575732	1.231954	2.326305
C	-3.664275	0.642372	2.970994
C	-3.787373	-0.746271	3.115350
C	-2.739770	-1.531353	2.622586
C	-1.669288	-0.970493	1.930444
C	-1.546253	0.432433	1.734749
O	-1.705813	2.643572	-0.608374
S	-2.224602	-1.686070	-4.076716
C	-2.108402	-2.482824	-2.470356
C	-2.783656	-3.697992	-2.322729
C	-2.684371	-4.415969	-1.135590
C	-1.941250	-3.914018	-0.072794
C	-1.287108	-2.688374	-0.210979
C	-1.290021	-1.936810	-1.427474
C	-6.979323	0.714451	-4.032480
C	-7.720649	0.197206	-2.798646
C	-8.196597	-1.139630	-2.769961
C	-8.119157	-2.025442	-3.999000
O	-1.334421	1.057985	-3.217915
S	-0.408574	-2.043317	1.220016
Tb	1.130568	0.046175	-0.184163
Br	-3.605084	-6.104032	-0.952243
O	-0.607552	-0.825145	-1.564859
C	-4.995839	-1.377264	3.792800

C	-6.261659	-1.398557	2.934320
C	-7.300490	-0.464758	3.183026
C	-7.257754	0.451884	4.390854
O	-0.564416	0.962166	1.042001
Br	-6.511472	6.230042	0.322771
S	5.196787	-3.992352	-0.880029
C	5.560307	-3.231857	0.724096
C	6.873102	-2.885174	1.065494
C	7.192507	-2.263296	2.275227
C	6.155466	-2.006315	3.178452
C	4.842692	-2.355505	2.871107
C	4.527569	-2.985049	1.648319
C	8.617298	-1.830957	2.606625
C	9.730168	-2.642669	1.984692
C	10.122301	-3.909709	2.545073
C	9.395078	-4.470898	3.746181
S	3.477806	-1.992482	3.996895
C	3.370578	-0.207168	3.786095
C	3.818301	0.599019	4.835937
C	3.780102	1.985742	4.713274
C	3.333519	2.582619	3.536175
C	2.899978	1.776128	2.485186
C	2.845483	0.351735	2.578625
Br	4.372405	3.089356	6.178468
S	2.322415	2.528168	0.955546
C	3.826196	2.566918	-0.052564
C	4.777905	3.553609	0.199158
C	5.932888	3.680311	-0.580863
C	6.071550	2.813001	-1.667108
C	5.123074	1.826442	-1.954998
C	3.969848	1.647602	-1.131569
C	6.986174	4.724686	-0.222156
C	7.964937	5.095067	-1.311286
C	9.234513	4.515269	-1.384650
C	9.732040	3.468021	-0.424333
S	5.313315	0.913272	-3.505491
C	6.117248	-0.624462	-3.020282
C	7.442141	-0.859048	-3.399445
C	8.036057	-2.083981	-3.100671
C	7.356945	-3.052233	-2.363349
C	6.041071	-2.811477	-1.951834
C	5.376035	-1.626719	-2.351387
O	4.074271	-1.475903	-2.099032
O	3.080713	0.692569	-1.367125
O	2.357974	-0.381624	1.618827
O	3.234206	-3.338967	1.384856
Br	9.843683	-2.424027	-3.674511
C	10.437905	-2.193771	0.865746
C	10.156948	-0.903572	0.144517
C	7.630348	6.064995	-2.318898
C	6.268153	6.719730	-2.328932
O	11.432116	-2.891878	0.363236
O	11.078072	-4.585391	2.059232
O	8.458233	6.397527	-3.221070
O	10.090455	4.858379	-2.320070
C	-6.398749	-2.380666	1.918119
C	-5.370677	-3.464854	1.732407
C	-7.962333	1.075497	-1.709305

C	-7.586536	2.532702	-1.776679
O	-7.392775	-2.435070	1.092522
Tb	-9.160884	-1.176305	0.461809
O	-11.490138	-1.012013	-0.449276
O	-8.349160	-0.329357	2.444056
O	-8.518610	0.715533	-0.598791
O	-8.739471	-1.696430	-1.741350
O	-10.402575	0.926441	1.272622
O	-9.437505	-3.676551	-0.075530
O	-10.692048	-2.349152	2.062307
H	7.992028	-0.085938	-3.938657
H	7.844153	-3.989392	-2.089141
H	4.608281	4.242654	1.033018
H	4.196786	0.132944	5.747370
H	3.317336	3.669100	3.433407
H	7.674256	-3.107229	0.356683
H	6.363657	-1.520110	4.135954
H	6.931709	2.914733	-2.334204
H	7.546346	4.361061	0.657385
H	6.463409	5.631111	0.130468
H	8.725597	-1.830794	3.705373
H	8.732465	-0.773994	2.310187
H	5.466477	5.964975	-2.299329
H	6.176977	7.332979	-3.234838
H	6.143769	7.365441	-1.443199
H	10.668640	3.047098	-0.814185
H	8.992210	2.664611	-0.289549
H	9.931080	3.912504	0.565242
H	9.081713	-0.682079	0.097274
H	10.557196	-0.978693	-0.876179
H	10.661177	-0.065061	0.655421
H	9.560727	-3.832622	4.630564
H	9.779962	-5.477969	3.952852
H	8.308851	-4.508248	3.568546
H	-4.970568	5.369624	-2.102278
H	-4.748934	4.638722	2.152834
H	-5.076316	-1.315889	-4.154528
H	-1.861680	-4.465780	0.865686
H	-3.378232	-4.076687	-3.155566
H	-4.420878	1.310569	3.391776
H	-2.752139	-2.615185	2.767914
H	-5.421279	2.959122	-3.696143
H	-7.205501	0.066820	-4.891788
H	-7.359598	1.711690	-4.309220
H	-5.199662	-0.838752	4.729629
H	-4.729527	-2.403013	4.097412
H	-6.507082	2.646132	-1.574485
H	-8.132780	3.088462	-1.002096
H	-7.781928	2.981452	-2.761191
H	-8.714612	-2.931324	-3.819138
H	-7.078763	-2.330772	-4.196671
H	-8.492361	-1.523389	-4.904664
H	-4.505919	-3.059650	1.178288
H	-5.797816	-4.280907	1.133641
H	-4.990716	-3.862414	2.684520
H	-7.009282	-0.084159	5.319405
H	-8.239849	0.931812	4.504112
H	-6.501710	1.242384	4.254677

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 H     9.546607     5.603421    -2.891605
 H    11.479384    -3.757666     1.002496
 H   -10.362709    -2.527303     2.963988
 H    -9.809663     1.433581     0.662260
 H    -8.513061    -3.786765     0.263247
 H   -11.598952    -0.772903    -1.389585
 H   -11.813652    -0.241479     0.067239
 H    -9.302554    -3.495227    -1.036342
 H   -10.756555    -3.222938     1.617969
 H    -9.890983     0.909906     2.116869
 H     2.718913    -2.929816     2.141481
 H    -1.041390     0.177927    -2.771287
 O     1.958651    -2.144097    -0.727460
 H     2.370871    -2.621057     0.044971
 O     0.706175     1.874607    -1.725737
 H    -0.157278     1.962871    -2.210893
 H     1.423834     1.860777    -2.389228
 H    -1.298113     2.206309     0.211838
 H     3.763303    -0.484420    -1.987206
 H     2.725460    -2.136900    -1.366469
```

Cartesian coordinates (in Å) for $[Tb(H_2O)_8]^{3+}$ optimized at the PBE/L1 level

```
  25
Tb(III) aquacomlex
   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 ligand ***2*** optimized at the PBE/L1 level

```
     48
Ligand 2
 C     1.723148     4.754748    -6.463122
 C     2.853188     4.149870    -5.920155
 C     2.757102     2.872840    -5.356499
```

C	1.518108	2.194753	-5.336622
C	0.384064	2.829371	-5.888815
C	0.489592	4.107802	-6.443208
S	4.187305	2.182328	-4.501723
C	4.953069	1.140844	-5.760161
C	4.546463	-0.201880	-5.919787
C	5.235673	-1.018540	-6.843565
C	6.299350	-0.497833	-7.588686
C	6.680207	0.830214	-7.418636
C	6.021068	1.649023	-6.504476
S	-1.241824	2.056560	-5.770467
C	-1.302469	1.004128	-7.233901
C	-1.946495	1.474613	-8.383515
C	-2.123416	0.628332	-9.474491
C	-1.675820	-0.690225	-9.433356
C	-1.025246	-1.168150	-8.292650
C	-0.830595	-0.326018	-7.176129
O	1.374202	0.959543	-4.797653
S	4.873830	-2.782412	-6.947235
C	3.543701	-2.856933	-8.163754
C	3.855688	-3.149595	-9.494133
C	2.833664	-3.297071	-10.429197
C	1.499638	-3.173780	-10.051199
C	1.176050	-2.887600	-8.720371
C	2.197664	-2.722837	-7.758898
O	3.513860	-0.661959	-5.172131
S	-0.555321	-2.908250	-8.215591
O	1.933970	-2.450101	-6.457734
O	-0.205531	-0.828611	-6.083603
H	3.813855	4.666522	-5.913254
H	-0.399951	4.589258	-6.851599
H	6.831440	-1.146050	-8.286221
H	0.698441	-3.313869	-10.778056
H	4.900370	-3.264763	-9.786103
H	-2.319135	2.499548	-8.406137
H	-1.831137	-1.359191	-10.280841
H	6.331452	2.684334	-6.357289
Br	8.142989	1.537152	-8.442604
Br	1.861963	6.508905	-7.232316
Br	-3.010990	1.280080	-11.047828
Br	3.270066	-3.693010	-12.256968
H	3.145049	-1.502628	-5.574350
H	2.268125	0.514228	-4.713315
H	1.000092	-2.099153	-6.361714
H	0.122817	-0.082307	-5.500737

Cartesian coordinates (in Å) for ligand ***5*** optimized at the PBE/L1 level

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   48
Ligand 5
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C	1.721557	4.772985	-6.429164
C	2.854837	4.164682	-5.897431
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C	1.526332	2.198987	-5.335662
C	0.388956	2.836916	-5.877796
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S	4.199640	2.182424	-4.510136

C	4.955321	1.144629	-5.777796
C	4.550710	-0.199623	-5.931590
C	5.230189	-1.018382	-6.861326
C	6.282311	-0.489523	-7.616825
C	6.674377	0.839391	-7.466051
C	6.013487	1.646532	-6.540279
S	-1.234723	2.057655	-5.768408
C	-1.292649	1.014005	-7.238495
C	-1.922982	1.484226	-8.395650
C	-2.104902	0.653221	-9.499643
C	-1.660947	-0.667712	-9.441810
C	-1.022621	-1.160323	-8.300375
C	-0.830787	-0.320130	-7.181602
O	1.386291	0.958125	-4.810542
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C	3.536068	-2.870908	-8.165181
C	3.846363	-3.182788	-9.491600
C	2.823267	-3.339029	-10.423711
C	1.489853	-3.204712	-10.048127
C	1.167322	-2.899413	-8.721250
C	2.190220	-2.726707	-7.762201
O	3.525241	-0.660971	-5.173033
S	-0.564715	-2.903459	-8.217712
O	1.928275	-2.437962	-6.464840
O	-0.214438	-0.827775	-6.085136
H	3.814414	4.683206	-5.886331
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H	6.800767	-1.147466	-8.317743
H	0.687650	-3.350510	-10.772689
H	4.890649	-3.305474	-9.781777
H	-2.284010	2.514986	-8.408449
H	-1.809166	-1.343306	-10.287167
H	6.315127	2.685614	-6.390797
H	7.499345	1.241053	-8.057691
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H	-2.601679	1.028970	-10.396285
Br	3.258194	-3.761504	-12.247878
H	3.155811	-1.501234	-5.574123
H	2.280971	0.512562	-4.729496
H	0.994737	-2.084420	-6.369662
H	0.115204	-0.081835	-5.503495

Cartesian coordinates (in Å) for ligand ***7*** optimized at the PBE/L1 level

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   80
Ligand 7
 C     0.023374    -1.952127    -2.298325
 C     1.246219    -2.491555    -1.842031
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 C     0.049672    -4.069133    -0.460567
 C    -1.167371    -3.557692    -0.902012
 C    -1.187035    -2.500935    -1.819006
 S     2.811873    -1.906182    -2.520898
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 C     3.206645     1.901995    -1.070983
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 C     1.199212     3.864042    -0.736331
 C     1.187403     4.569047     0.472361
 C    -0.025212     4.913277     1.062207
 C    -1.233721     4.572604     0.459429
 C    -1.234185     3.862357    -0.744138
 C    -0.015466     3.500208    -1.360048
 S    -2.807286     3.527482    -1.561589
 C    -3.187612     1.840774    -1.044070
 C    -4.033042     1.629504     0.048238
 C    -4.469539     0.349199     0.408490
 C    -4.045916    -0.726440    -0.377006
 C    -3.193654    -0.547147    -1.470339
 C    -2.749685     0.744310    -1.819821
 S    -2.765956    -1.963309    -2.504991
 C    -5.360594     0.162153     1.633683
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 O    -1.930342     0.890654    -2.891925
Br    -0.032845     5.883961     2.721877
 O    -0.056647     2.826518    -2.533657
 C     5.419564     0.256526     1.591517
 C     6.119287    -1.074242     1.727672
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 O     1.921907     1.020656    -2.876015
Br     0.068574    -5.518995     0.801749
 O     0.055682    -0.931592    -3.188807
 C    -7.383273    -1.291465     1.000934
 O    -8.051339    -2.366333     1.076237
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 C     5.606525    -2.091796     2.538909
 O     6.231463    -3.237925     2.672017
 C     4.325392    -1.973923     3.319534
 C    -4.413273    -2.212539     3.260097
 C     7.967232    -0.308575     0.125747
 H     2.208092    -3.965948    -0.601483
 H    -2.110931    -3.981461    -0.555327
 H     4.412332     2.583239     0.561649
 H    -2.184306     4.857637     0.912108
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H	2.134032	4.856473	0.931765
H	-4.396306	-1.735976	-0.147107
H	-4.367468	2.502267	0.617229
H	4.419320	-1.665036	-0.145652
H	4.817412	0.445530	2.497459
H	6.165853	1.069736	1.571955
H	-6.053248	1.020323	1.684045
H	-4.726733	0.255049	2.532807
H	7.240026	0.048762	-0.620268
H	8.835310	-0.752531	-0.378472
H	8.299586	0.567273	0.708182
H	4.056948	-2.963711	3.712150
H	3.505377	-1.590020	2.694380
H	4.452536	-1.282842	4.169714
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H	-4.212300	-3.233933	3.609862
H	-4.501764	-1.552537	4.139275
H	-8.204610	0.693951	0.773080
H	-8.829329	-0.532932	-0.373989
H	-7.184992	0.172769	-0.584703
H	7.110224	-3.117158	2.045746
H	-7.253596	-3.121699	1.923080
H	-1.465112	1.775630	-2.842272
H	0.825645	2.384447	-2.715944
H	1.459091	0.168121	-3.125772

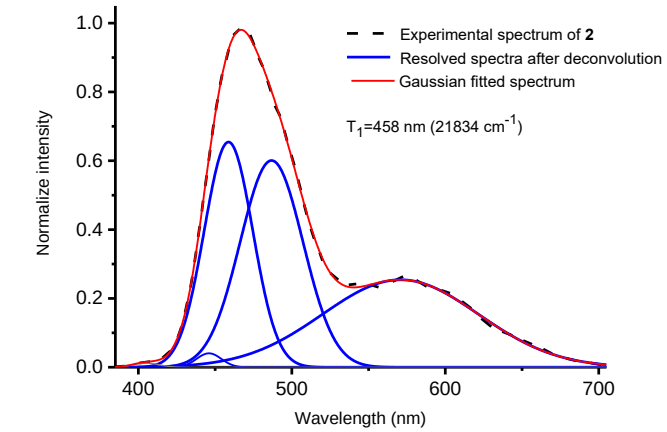
6. Parameters of two-exponential expansion fittings luminescence decay curves of Tb^{3+} complexes in DMF solutions

Table S3. Parameters of two-exponential expansion fitting luminescence decay curves of DMF solutions of Tb^{3+} (0.1 mM) after the addition of L (0.1mM) and TEA (0.8 mM) (normalized data) at 298 K (323 K).

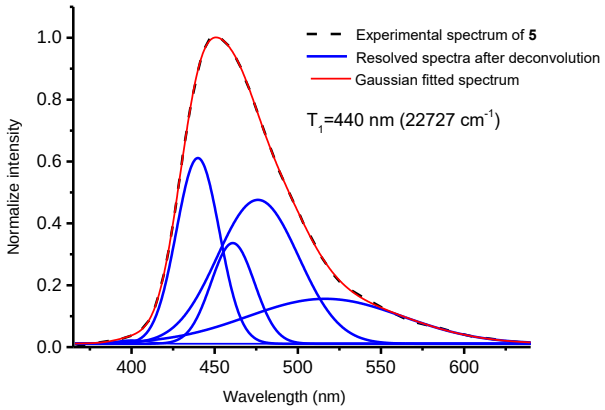
$Tb^{3+}{}_2L_2$	T, K	λ_{ex} (nm)	A_1	τ_1(μs)	A_2	τ_2 (μs)	<τ> (μs)	Goodness-of-fit parameter χ^2, 10^{-6}	R^2
1	298	348	0.436±0.008	664±5	0.566±0.008	1266±5	1090	0.65	0.99997
2	298	360	0.424±0.021	1206±15	0.573±0.021	701±8	980	1.77	0.99991
	323		0.387±0.011	1099±13	0.619±0.011	445±5	842	8.30	0.99944
5	298	330	0.693±0.004	1226±3	0.297±0.004	491±4	1120	1.37	0.99993
	322		0.454±0.015	1208±12	0.545±0.015	642±7	990	2.25	0.99988
7	298	350	0.405±0.006	521±4	0.586±0.006	1188±5	1030	1.66	0.99991
	323		0.552±0.012	1105±9	0.450±0.012	484±7	940	5.97	0.99966

7. The determination of the T_1 state energy of the ligands 2, 5 and 7 in their Gd^{3+} complexes

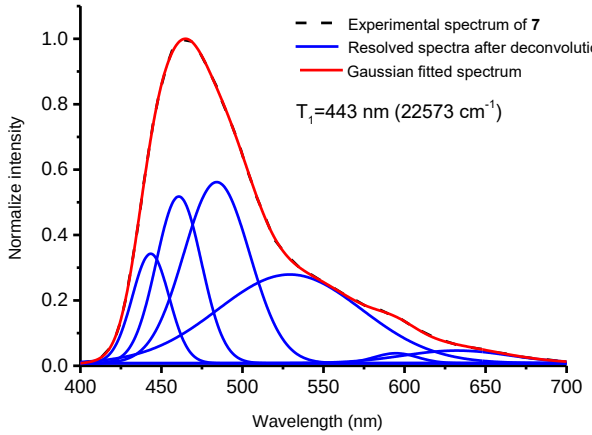
The phosphorescence spectra of the Gd^{3+} complexes **2** (a), **5** (b) and **7** (c) at 146 K and 30 μs time delay are characterized by broad bands with maxima at 468 nm (21367 cm^{-1}), 450 nm (22222 cm^{-1}) and 465 nm (21505 cm^{-1}), respectively (Figure S12). Since these spectra do not contain a fine vibrational structure, required to accurate determination of the position of the maximum of the 0–0 phonon transition corresponding to the energy of the T_1 of the state of the ligands, we used a spectral deconvolution of the spectra into a series of overlapping bands using a Gaussian function [S. Shuvaev, V. Utochnikova, Ł. Marciniak, A. Freidzon, I. Sinev, R. Van Deun, R.O. Freire, Y. Zubavichus, W. Grünert and N. Kuzmina, Dalton Trans., 2014, **43**, 3121-3136; Xian-Sheng Ke, Bo-Yan Yang, Xin Cheng, Sharon Lai-Fung Chan, and Jun-Long Zhang, Chem. Eur. J. 20 (2014) 4324-4333]. Energies values of the T_1 states of the ligands were determined from the maxima of short-wavelength deconvoluted bands. The values for the Gd^{3+} complexes **2** (a), **5** (b) and **7** (c) are 458 nm (21834 cm^{-1}), 440 nm (22727 cm^{-1}) and 452 nm (22124 cm^{-1}), respectively.



a



b



c

Figure S11. A spectral deconvolution of the normalized phosphorescence spectra of the Gd^{3+} complexes **2** (a), **5** (b) and **7** (c) at 30 μs time delay and T = 146 K into subcomponent by using a Gaussian curve fitting.

8. **Parameters of three-exponential expansion fitting phosphorescence decay curves of Gd^{3+} complexes with the ligands 2, 5 and 7**

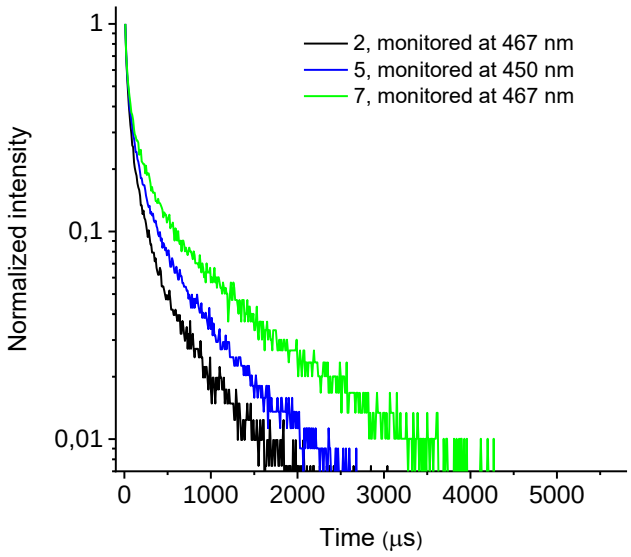


Figure S12. Normalized phosphorescence decay curves (λ_{exc}=337 nm) of the alkalized DMF solutions of Gd^{3+} complexes with the ligands **2** (λ_{max}=467 nm), **5** (λ_{max}= 450 nm) and **7** (λ_{max}= 467 nm) at T=146 K. $C_L = C_{Gd3+}$ = 1 mM, C_{TEA} = 4 mM.

The values of the lifetime (τ) of the Gd^{3+} complexes with the ligands **2**, **5** and **7** were evaluated from the phosphorescence decay curves (Fig. S10) on the basis of three-exponential expansion:

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

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.

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

Table S4. Parameters of three-exponential expansion fittings for luminescence decay curves of the Gd^{3+} complexes at 146 K (Normalized data).

Complex Gb^{3+}- **L**	A_1	τ_1 (μs)	A_2	τ_2 (μs)	A_3	τ_3 (μs)	$<\tau>$ (μs)	Goodness-of-fit parameter χ^2, 10^{-6}	R^2	λ_{em} (nm)
2	0.9±0.01	15±0.4	0.5±0.01	89±2	0.1±0.003	545±13	301	7.4	0.9988	467
5	0.9±0.01	15±0.3	0.4±0.005	109±2	0.1±0.002	696±10	421	6.2	0.9990	450
7	0.9±0.01	15±0.4	0.4±0.01	138±3	0.2±0.003	1013±20	785	16	0.9978	467

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

9. Luminescence spectra of the terbium complexes with ligands 2 and 5.

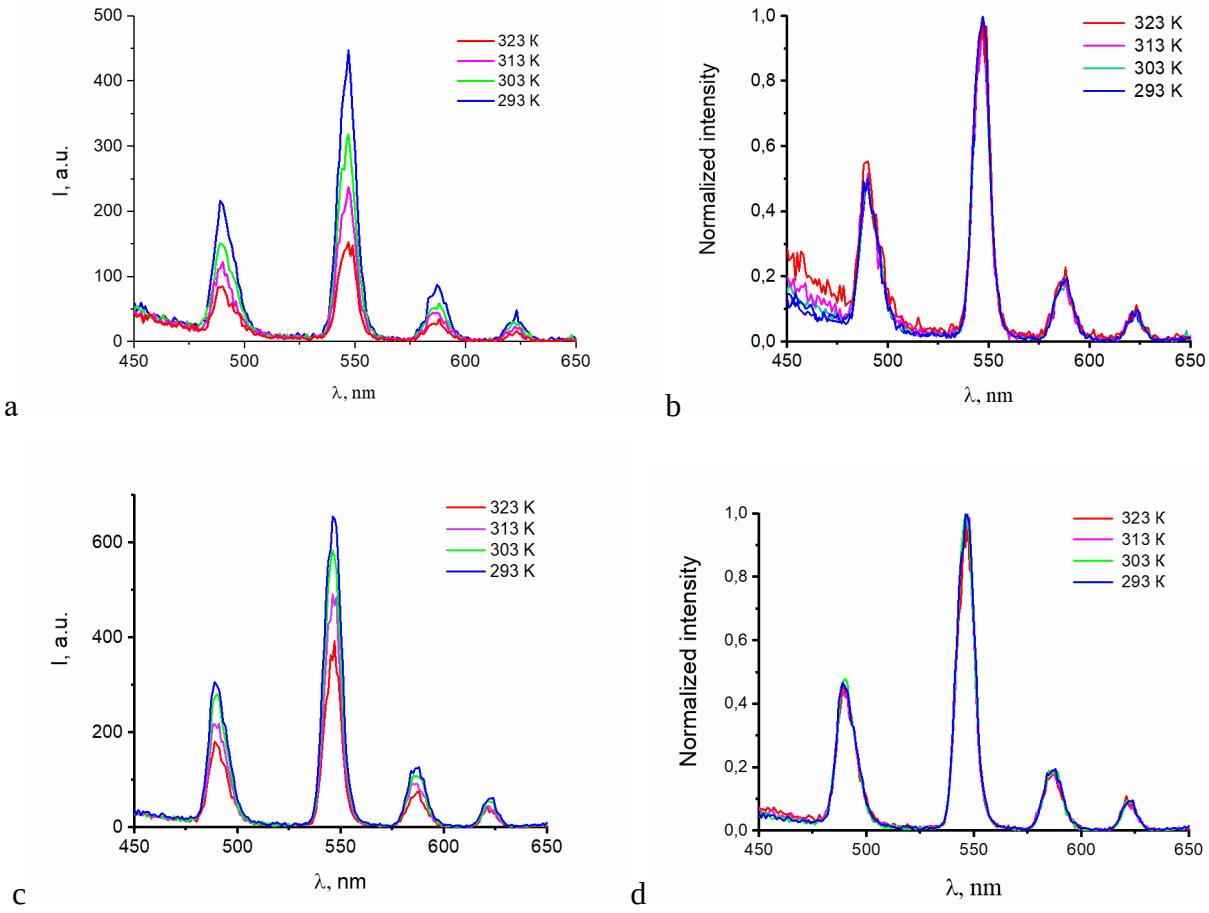


Figure S13. The Tb^{3+}-centered luminescence spectra (a, c) and normalized spectra (b, d) recorded at the various temperatures for terbium complexes with ligands **2** (a, b) (λ_{ex} = 350 nm) and **5** (c,d) (λ_{ex} = 346 nm) in alkaline DMF solutions. $C_{Tb^{3+}} = C_L$ = 0.1 mM, L:Tb^{3+}:TEA (1:1:8).

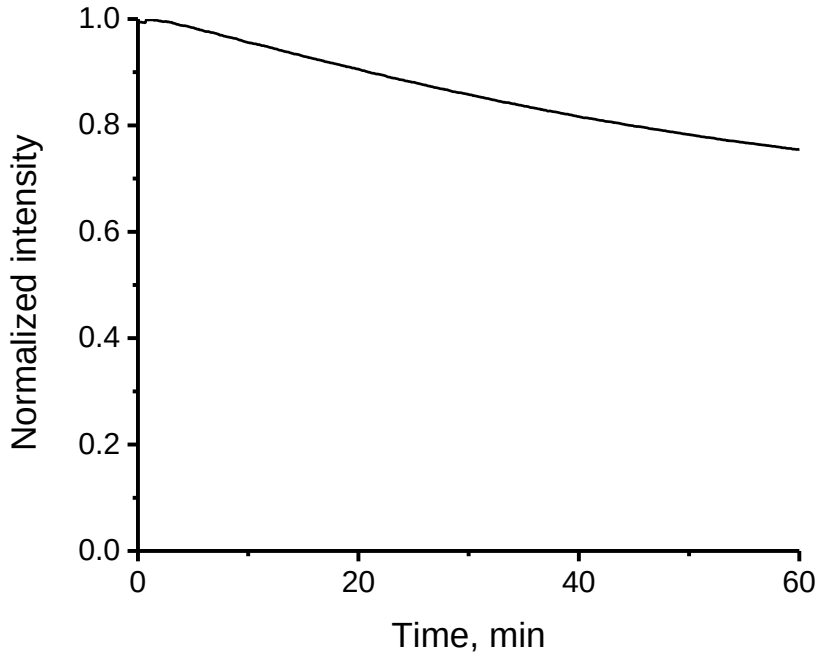


Figure S14. The change in time of normalized luminescence intensity at 545 nm of the terbium complexes with ligands **2** at UV- irridation (λ = 350 nm) in alkaline DMF solutions. $C_{Tb}^{3+} = C_L$ = 0.1 mM, L:Tb^{3+}:TEA (1:1:8), T = 21 ºC.