Supplementary Material (ESI) for Chemical Communications

Supporting Information

First direct assembly of molecular helical complexes to coordination polymer

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I. Materials and apparatus

Suchanil chloride, 1-phenyl-3-methylpyrazol-5-on, dioxane, ethanol, Tb_4O_7, rodamin B were obtained from Aldrich Chemical Company Ltd. or Fluka and used without further purification. Lanthanide nitrates were obtained from corresponding oxides.

Chemical analyses of the samples dried to constant weight were performed with a Fisons Instruments 1108 CHNS-O Elemental analyzer. IR spectra in the range 4000–400 cm^{-1} were recorded on a Perkin–Elmer System 2000 FT-IR spectrometer. 300 MHz ^1H NMR spectra were measured using a VXR-300 Varian spectrometer operating at room temperature. Proton chemical shifts are reported in ppm using $(CH_3)_4Si$ as reference. MALDI-TOF mass spectra were recorded on Bruker Daltonics Ultraflex II with matrix DCTB (trans-2-[3-(4-tert-Butyl(phenyl)-2-methyl-2-propenyliden)malonnitrile (0.1M in DCM). A quantum yield of the ethanolic solution of **1** was obtained using PerkinElmer LS50B spectrometer and was calculated by standard technique, using equation $\varphi_X = \frac{n_X^2 A_{ref} I_X}{n_{ref}^2 A_X I_{ref}} \varphi_{ref}$, were n – refractive index, A – absorbance of solution, I – luminescent intensity. In our measurements all solutions have the same absorbance $A_{ref} = A_x = 0.15$, $n_x = n_{ref}$ because we have diluted solutions in same solvent (ethanol). X-ray diffraction patterns for **3** were recorded on a PHILIPS PW1820 diffractometer (PANalytical, The Netherlands) with CuKα radiation (λ = 1.54056 Å) with automatic divergence slit and a secondary graphite monochromator at room temperature.

II. Single-crystal X-ray structure determination

Data collection for crystals of **1 - 3** was carried out on Stoe IPDS diffractometer (Imaging Plate Detector System with graphite-monochromated MoK_α radiation, λ = 0.71073 Å) at 183(2) or 100(2) K using a cold N_2-gas stream. Direct method was used to solve the crystal structure of **2** and **3** and Paterson method was used for **1** by means of SHELXS-97 program [1]. The structure refinement was performed with the program SHELXL-97. Non-hydrogen atoms were refined anisotropically by full-matrix least-squares techniques based on F^2. The hydrogen atoms of organic groups were placed in calculated positions and refined in a riding mode with a fixed temperature factor. Hydrogen atoms of the crystal water molecules O43 – O50 in structure of **1** were not considered. Two phenyl rings in **2** have been found to be disordered over two positions with same

occupancy. They were refined with help of AFIX and EADP procedures in the frame of SHELXL-97 program.

III. Synthesis

Bis-4-(1-phenyl-3-methylpyrazol-5-on)butadione-1,4 (H_2Q_2Q) was obtained by procedure described in [2]. Diphenylphosphinethane dioxide ($dppeO_2$) was synthesized by oxidation of diphenylphosphinethane (dppe) by hydrogen peroxide in THF [3].

$[Tb_2(Q_2Q)_3(H_2O)_2]$ (1): To an ethanol solution (10 ml) of the ligand H_2Q_2Q (0.108 g, 0.25 mmol) in the presence of the two equivalents of Et_3N (0.050 g, 0.5 mmol), an ethanol solution (5 ml) of $Tb(NO_3)_3{\cdot}6H_2O$ (0.0757 g, 0.167 mmol) was added under refluxing. The resulting mixture was refluxed for 30 minutes. The resulting white precipitate was separated by filtration and washed with ethanol, to give 0.157 g of pure $[Tb_2(Q_2Q)_3(H_2O)_2]\cdot(H_2O)_{7/3}(C_2H_5OH)_{1/3}$**.** Yield ~85%. Anal. Calc. for $Tb_2C_{72}H_{64}N_{12}O_{14}(H_2O)_{7/3}(C_2H_5OH)_{1/3}$: C, 51.39; H, 4.17; N, 9.90. Found: C, 50.89; H, 4.01; N, 9.73%. IR (Nujol, cm^{-1}) 3600 (O-H...O), 3350 (O-H), 1621, 1594, 1533 (C=O, C=C, C=N), 1072, 1032, 1003, 946, 846. ^1H NMR (DMSO d^6, 200 MHz): -9.6, -5.83, -3.31, 1.06, 4.21, 7.35, 8.62, 14.91, 16.09, 17.65, 18.57. MALDI-MS (m/z) 1623 $[Tb_2(Q_2Q)_3+Na]^+$.

The single crystals suitable for X-ray structural analysis have been grown in accordance with following technique: H_2Q_2Q (20 mg), Et_3N (10 mg) and $Tb(NO_3)_3{\cdot}6H_2O$ (15 mg) were mixed in 8 ml of ethanol. The resulting mixture was placed into autoclave with teflon liner and heated up to 140 ^oC. Cooling of this mixture to room temperature during three days lead to well-shaped crystals of **1**.

$[Tb_2(Q_2Q)_3(DMF)_2]$ (2): The **1** (40 mg) was dissolved in 2 ml of DMF at room temperature. The resulting solution was stand at 40^oC during two hours and 1 ml of ethanol was added. After 8 hours, desired product was precipitated as crystalline powder and washed with ethanol, to give 25 mg of **2**. Yield ~60%**.** Anal. Calc. for $Tb_2C_{78}H_{77}N_{14}O_{14}$: C, 53.46; H, 4.40; N, 11.19. Found: C, 53.28; H, 4.53; N, 11.35%. IR (Nujol, cm^{-1}): 1667 (C=O DMF),1612, 1592, 1581, 1531 (C=O, C=C, C=N), 1180, 1159 (P=O), 1075, 1032, 1001, 992, 842. MALDI-MS (m/z) 1623 $[Tb_2(Q_2Q)_3+Na]^+$.

The single crystals suitable for X-ray structural analysis have been grown in accordance with following technique: the -20 mg 20g of **1** was dissolved in mixture of 1 ml DMF with 0.3 ml $Si(OMe)_4$ and one drop of water with 1/3 drop of hydrofluoric acid were added. Heating up to 60 ^oC during 2 days followed by slow cooling to room temperature resulted in well-shaped crystals of **2** in gel.

$[Tb_2(Q_2Q)_3(dppeO_2)]_n$ (3) This compound was prepared using the same procedure as it was applied for 1 witn presence of stoichiometric amount (36 mg, 0.084 mmol) of $dppeO_2$. After refluxing of reaction mixture, microcrystalline precipitate of 3 has been obtained. Yield ~80%**.** Anal. Calc. for $Tb_2C_{98}H_{87}N_{12}O_{14}P_2$: C, 57.88; H, 4.16; N, 8.27. Found: C, 57.91; H, 4.20; N, 8.23%. IR (Nujol, cm^{-1}) 1615, 1594, 1532 (C=O, C=C, C=N), 1180, 1159 (P=O), 1074, 1032, 991, 840. MALDI-MS m/z 2032 $[M+H]^+$, 1623 $[Tb_2(Q_2Q)_3+Na]^+$.

The single crystals suitable for X-ray structural analysis have been grown in accordance with following technique: the 20 mg of **1** was dissolved in 1 ml of DMF and $dppeO_2$ (5 mg) was added. Heating of resulting solution up to 70 ^oC during two weeks resulted in prismatic crystals of **3.**

IV. X-Ray powder diffraction.

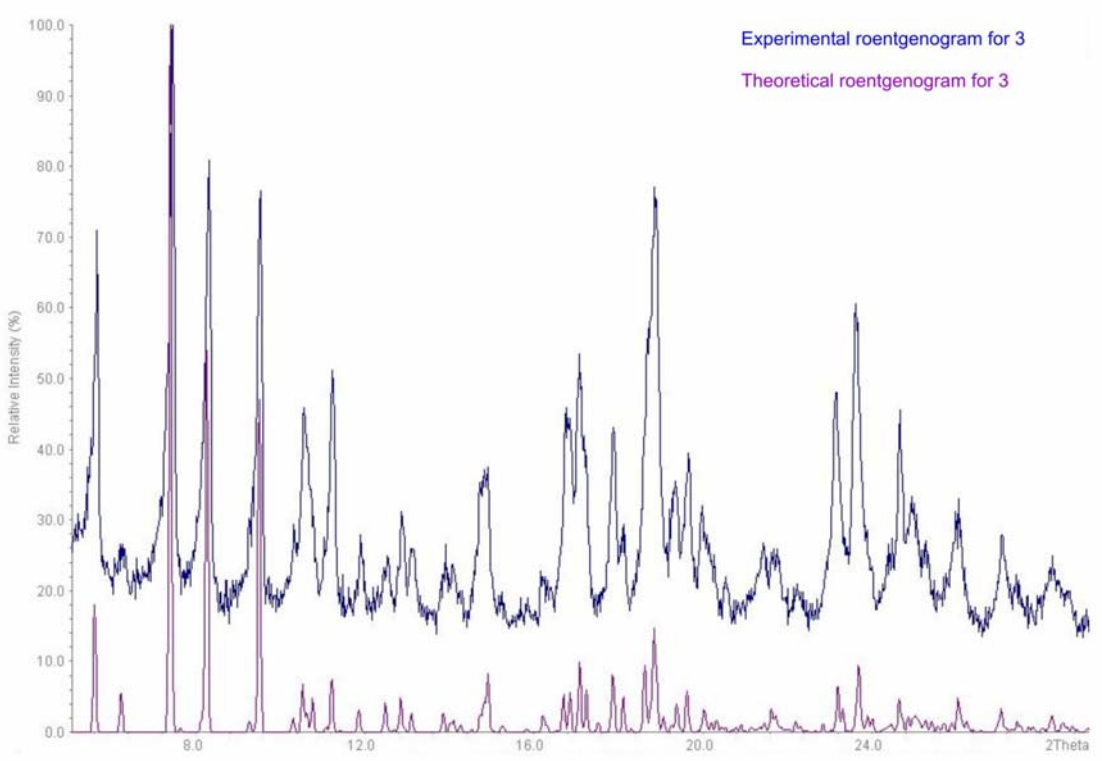

Figure S1. Correlation between theoretical (calculated from single crystal data) and experimental powder roentgenograms for **3**.

V. Crystal structures details for 1 – 3.

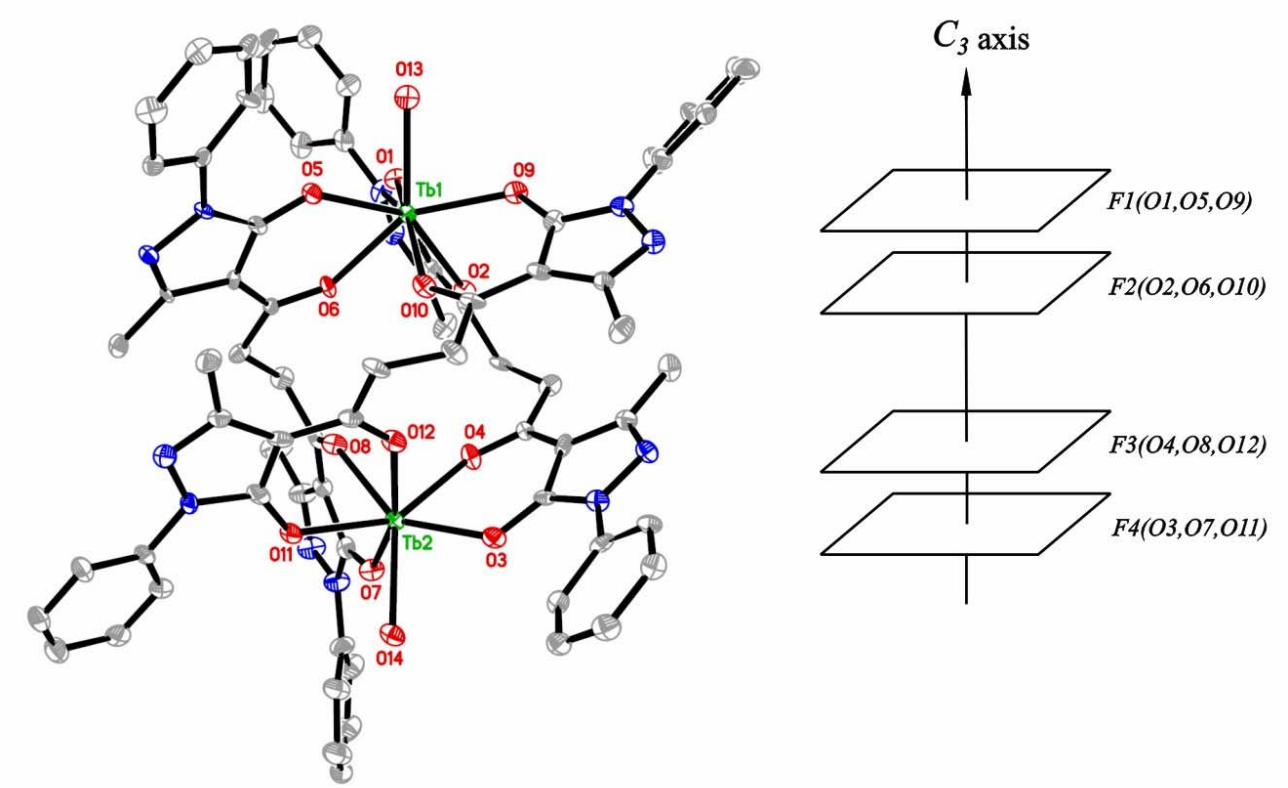

Figure S2. Facial planes F1 – F4 delimiting the helical portions in **1 – 3**, each plane was defined by the three oxygen atoms and approximately perpendicular C_3-axis of helix.

The piths P_{ij} were defined by equation $P_{ij} = d(F_i – F_j)/(360/ \omega_{ij})$ [4], in which $d(F_i – F_j)$ is separation between facial planes and ω_{ij} is the average twist angle defined by the angular rotation between projection of oxygen atoms belonging to the same ligand.

Table S1. Helical pitches P_{ij}, linear distances $d(F_i - F_j)$ and average twist angles ω_{ij} along the pseudo-C_3 axis in the crystal structures of $[Tb_2(Q_2Q)_3(H_2O)_2]$, $[Tb_2(Q_2Q)_3(DMF)_2]$ and $[Tb_2(Q_2Q)_3(dppeO_2)]_n$.

Part	**$[Tb_2(Q_2Q)_3(H_2O)_2]$**[1]			**$[Tb_2(Q_2Q)_3(DMF)_2]$**		
	$d(F_i - F_j)$ [Å]	ω_{ij} [º]	P_{ij} [Å]	$d(F_i - F_j)$ [Å]	ω_{ij} [º]	P_{ij} [Å]
F1 – F2	1.956	59.7	11.8	2.055	55.8	12.9
F2 – F3	3.111	13.3	84.2	3.211	13.4	86.3
F3 – F4	1.944	59.4	11.8	1.995	58.0	12.4
	$[Tb_2(Q_2Q)_3(dppeO_2)]_n$					
	$d(F_i - F_j)$ [Å]	ω_{ij} [º]	P_{ij} [Å]			
F1 – F2	2.042	55.7	13.2			
F2 – F3	3.321	12.3	97.6			
F3 – F4	1.952	59.4	11.8			

[*1*] *An average values for tree crystallographic independent molecules are presented.*

Table S2. An angles between facial planes $\angle F_i F_j$ and average angles $\angle TbTbO_{ter\,min\,al}$, were $O_{terminal}$ is oxygen atom from additional ligand, in the crystal structures of $[Tb_2(Q_2Q)_3(H_2O)_2]$, $[Tb_2(Q_2Q)_3(DMF)_2]$ and $[Tb_2(Q_2Q)_3(dppeO_2)]_n$.

	$[Tb_2(Q_2Q)_3(H_2O)_2]$	**$[Tb_2(Q_2Q)_3(DMF)_2]$**	**$[Tb_2(Q_2Q)_3(dppeO_2)]_n$**
$\angle TbTbO_{ter\,min\,al}$, [º]	167	172	175
$\angle F1F2$, [º]	3.72	2.32	2.66
$\angle F2F3$, [º]	4.81	3.10	2.23
$\angle F3F4$, [º]	7.51	6.67	4.74

Table S3. Selected bond lengths (Å) in the crystal structure of $[Tb_2(Q_2Q)_3(H_2O)_2]$

Tb1 – Tb2	6.186(1)	Tb4 – O17	2.293(7)
Tb1 – O1	2.267(6)	Tb4 – O18	2.363(6)
Tb1 – O2	2.343(6)	Tb4 – O21	2.323(6)
Tb1 – O5	2.289(6)	Tb4 – O22	2.314(6)
Tb1 – O6	2.343(6)	Tb4 – O25	2.306(5)
Tb1 – O9	2.303(6)	Tb4 – O26	2.327(6)
Tb1 – O10	2.322(6)	Tb4 – O28	2.317(6)
Tb1 – O13	2.340(7)	Tb5 – Tb6	6.052(1)
Tb2 – O3	2.265(6)	Tb5 – O29	2.286(6)
Tb2 – O4	2.330(6)	Tb5 – O30	2.352(6)
Tb2 – O7	2.291(7)	Tb5 – O33	2.315(7)
Tb2 – O8	2.334(6)	Tb5 – O34	2.345(6)
Tb2 – O11	2.280(6)	Tb5 – O37	2.292(6)
Tb2 – O12	2.344(7)	Tb5 – O38	2.307(6)
Tb2 – O14	2.369(7)	Tb5 – O41	2.349(6)
Tb3 – Tb4	6.087(1)	Tb6 – O31	2.307(6)
Tb3 – O15	2.272(6)	Tb6 – O32	2.323(6)
Tb3 – O16	2.312(6)	Tb6 – O35	2.299(6)
Tb3 – O19	2.329(6)	Tb6 – O36	2.332(6)
Tb3 – O20	2.333(7)	Tb6 – O39	2.308(6)
Tb3 – O23	2.285(5)	Tb6 – O40	2.317(6)
Tb3 – O24	2.338(6)	Tb6 – O42	2.333(6)
Tb3 – O27	2.353(7)		

Table S4. Selected bond lengths (Å) in the crystal structures of $[Tb_2(Q_2Q)_3(DMF)_2]$ and $[Tb_2(Q_2Q)_3(dppeO_2)]_n$.

	$[Tb_2(Q_2Q)_3(DMF)_2]$	**$[Tb_2(Q_2Q)_3(dppeO_2)]_n$**
Tb1 – Tb2	6.224(1)	6.333(1)
Tb1 – O1	2.294(5)	2.288(6)
Tb1 – O2	2.330(5)	2.350(6)
Tb1 – O5	2.301(5)	2.289(6)
Tb1 – O6	2.331(5)	2.328(5)
Tb1 – O9	2.292(5)	2.319(6)
Tb1 – O10	2.312(5)	2.345(6)
Tb1 – O13	2.327(6)	2.332(5)
Tb2 – O3	2.283(5)	2.291(5)
Tb2 – O4	2.336(5)	2.328(6)
Tb2 – O7	2.258(5)	2.343(5)
Tb2 – O8	2.365(5)	2.342(6)
Tb2 – O11	2.284(5)	2.286(6)
Tb2 – O12	2.359(6)	2.310(5)
Tb2 – O14	2.329(6)	2.324(5)

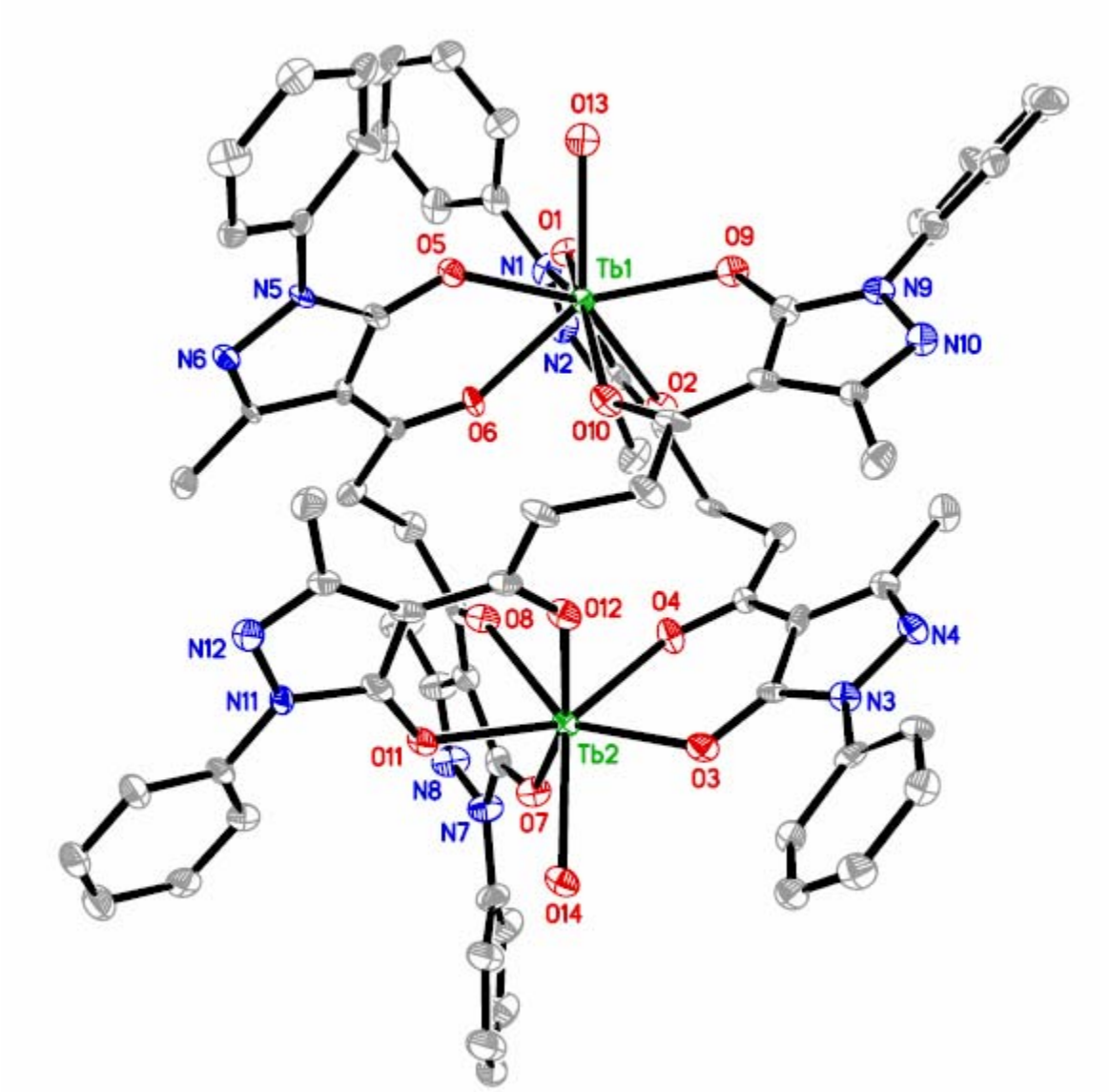

Figure S3. ORTEP drawing of [$\mathbf{Tb_2(Q_2Q)_3(H_2O)_2}$] (50% probability level of thermal ellipsoids). Only one of three crystallographic independent molecules is presented. The hydrogen atoms are omitted for clarity.

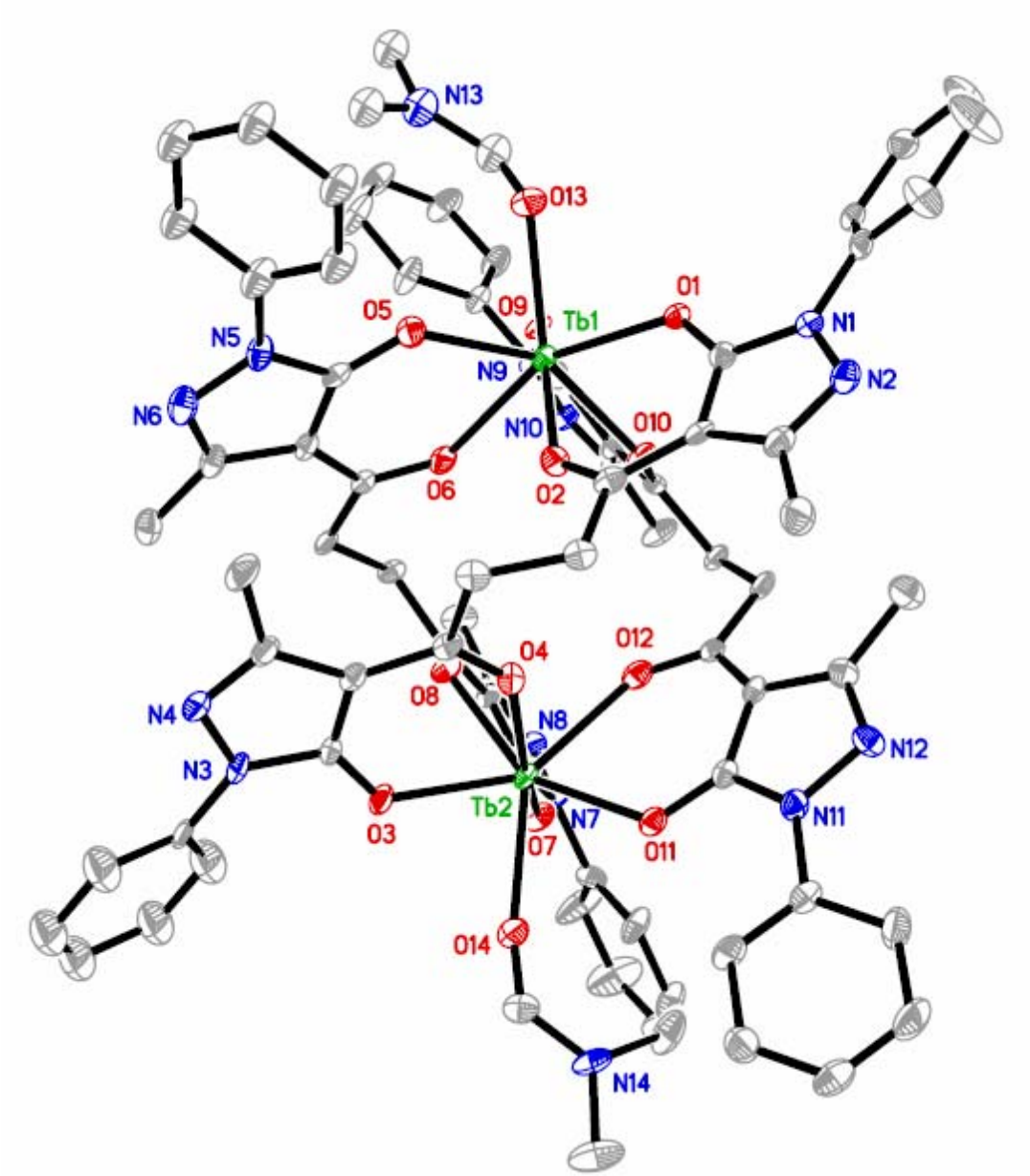

Figure S4. ORTEP drawing of [$\mathbf{Tb_2(Q_2Q)_3(DMF)_2}$] (30% probability level of thermal ellipsoids, for disordered phenyl rings only one position is presented). The hydrogen atoms are omitted for clarity.

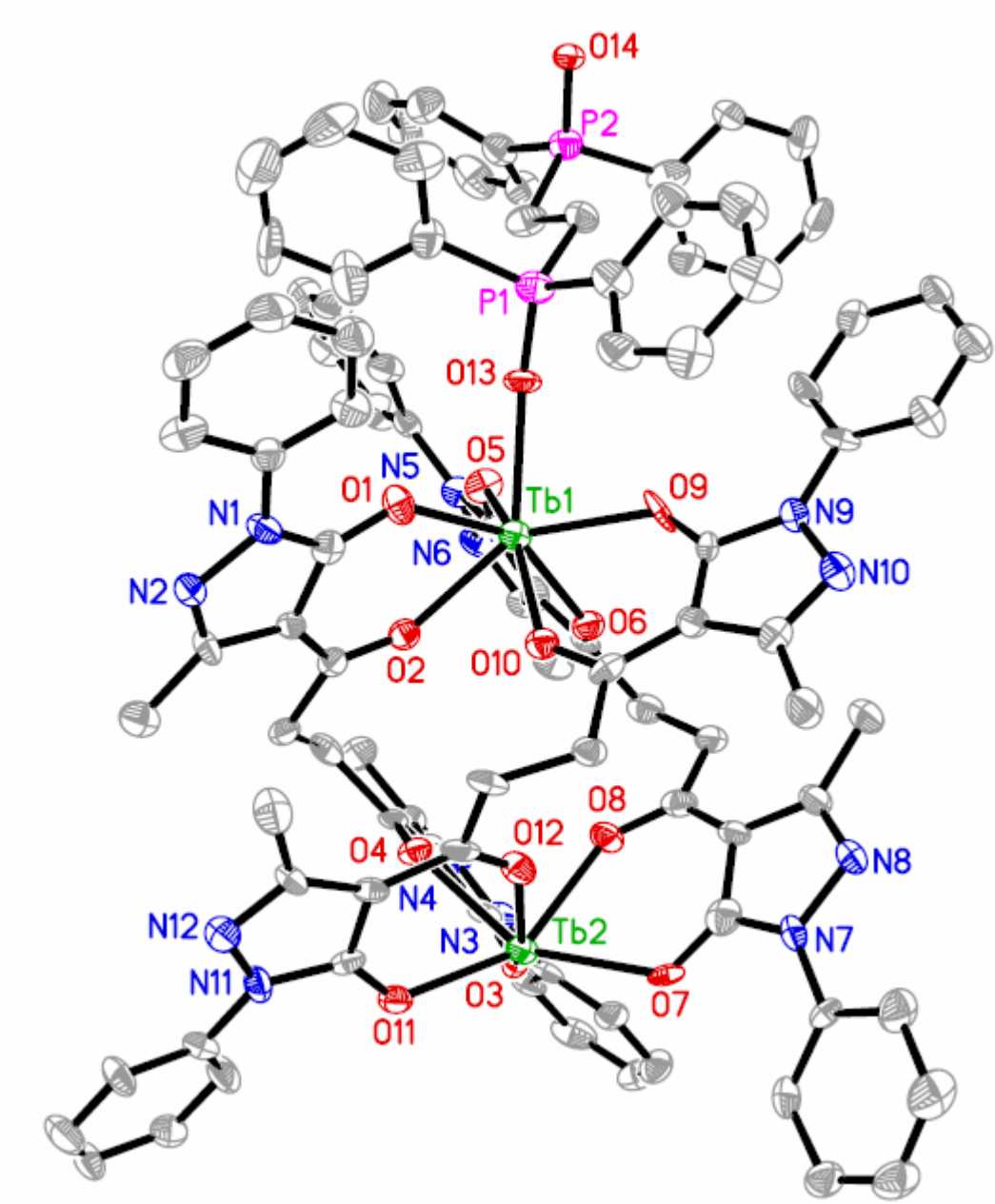

Figure S4. ORTEP drawing of crystallographic independent chain part in **$[Tb_2(Q_2Q)_3(dppeO_2)]_n$** (30% probability level of thermal ellipsoids). The hydrogen atoms are omitted for clarity.

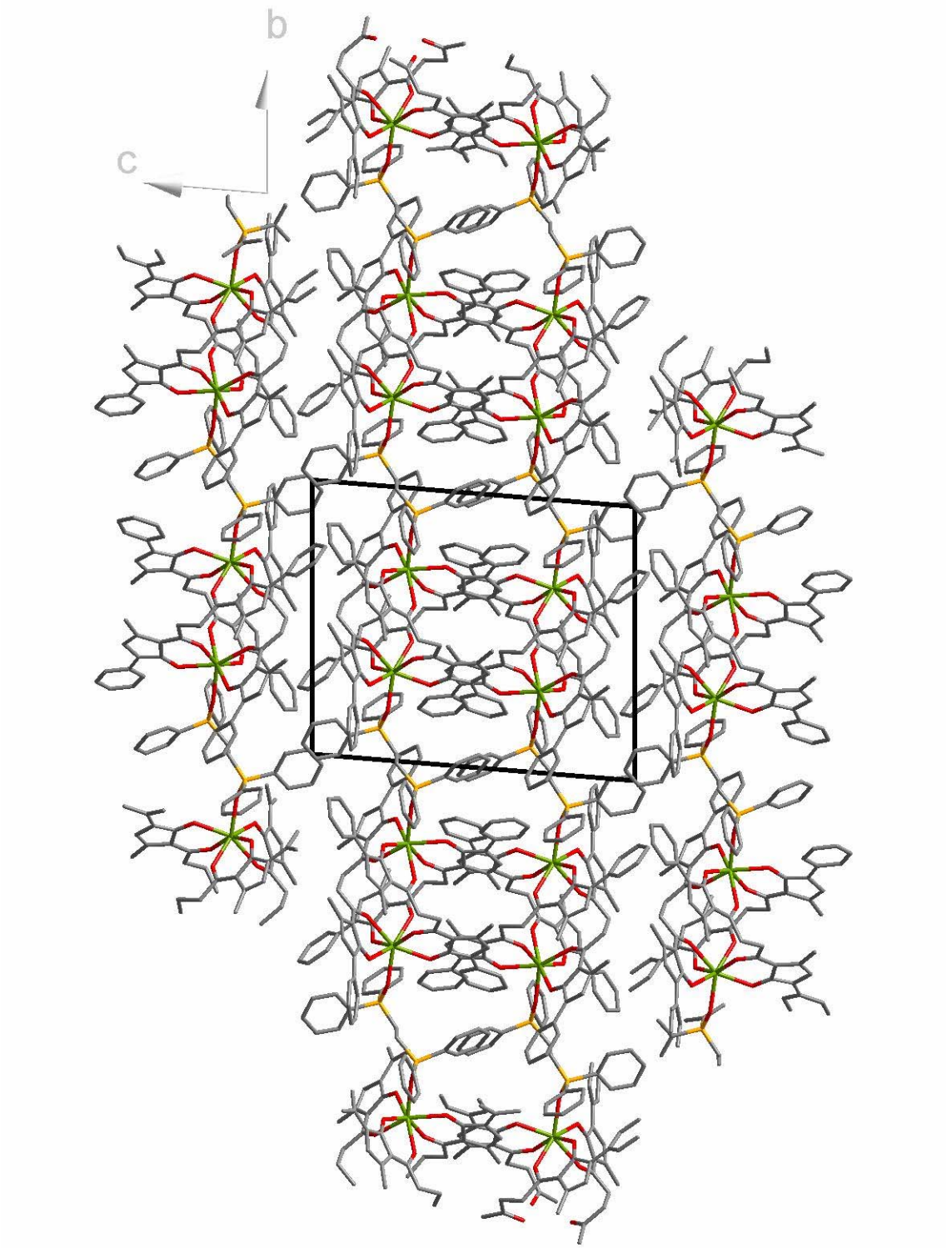

Figure S5. Crystal packing diagram for $\mathbf{[Tb_2(Q_2Q)_3(dppeO_2)]_n}$ (projection along ***a*** axis).

VI. Calculation details

The geometry of molecular structures were optimized at the DFT level of theory using the Perdew88/Becke86 gradient corrected functional (BP86) as it is implemented in TURBOMOLE 5.9 program package [5] comprising local density approximation [6], but adding non-local corrections to exchange [7] and correlation [8]. Since the terbium ion has strong interaction between spin and angular momentums, it has been replaced by the gadolinium ion. The chemical properties as well as ionic radii of terbium and gadolinium ions are quite similar (r(Tb(III)) = 1.063 Å and r(Gd(III)) = 1.078 Å for CN=6, r(Tb(III)) = 1.180 Å and r(Gd(III)) = 1.193 Å for CN=8) that makes this replacement applicable for modeling of chemical features of complexes of these metals. Since it is well-known that the *f*-electrons do not participate in chemical bonding [9], the Stuttgart-Bonn relativistic large-core effective core potential (RECP) with 53 core electrons has been used for gadolinium ions [10]. The valence electron shells of Gd-ion have been described by means of corresponding split valence quality basis set with contraction scheme as (7s6p5d)/[5s4p3d]. All other atoms of organic ligands have been described using split valence quality basis sets described in terms of TURBOMOLE nomenclature as def-SV(P) and corresponding to the following contraction schemes: for C – (7s4p1d)/[3s2p1d], for O – (7s4p1d)/[3s2p1d], for N – (7s4p1d)/[3s2p1d] and for H – (4s)/[2s]. In [11], it was mentioned that these level of basis sets is recommended for geometry optimization at the DFT/BP86 level as compromising between good reproducing of geometry features of metal complexes and time- and computer power costs.

To speed up calculations, the Resolution-of-Identity (RI) approximation has been applied. TURBOMOLE provides three types of auxiliary basis sets for RI-approximation. For our purposes, the Coulomb-Fitting ($jbas) basis sets approximating only the Coulomb part of the Fock operator have been chosen. The auxiliary basis sets used are following: for Gd (def-SVP) – (18s7p6d6f6g3h5i)/[14s7p6d6f5g2h2i], for C (def-SV(P)) – (8s3p3d1f)/[6s3p3d1f], for O (def-SV(P)) – (8s3p3d1f)/[6s3p3d1f], for N (def-SV(P)) – (8s3p3d1f)/[6s3p3d1f] and for H (def-SV(P)) – (4s2p)/[2s1p]. No symmetry constrains have been used for all systems under consideration (C_1 point group). Real harmonic frequencies indicated that the true minimum on the potential energy surface has been achieved. Optimized geometries were analyzed and visualized with help of the ChemCraft [12] and Molekel 5.2.0 [13] programs.

VII. Theoretical modeling of dihydrated helical complex of Gd, $[Gd_2(Q_2Q_3)_3(H_2O)_2]$

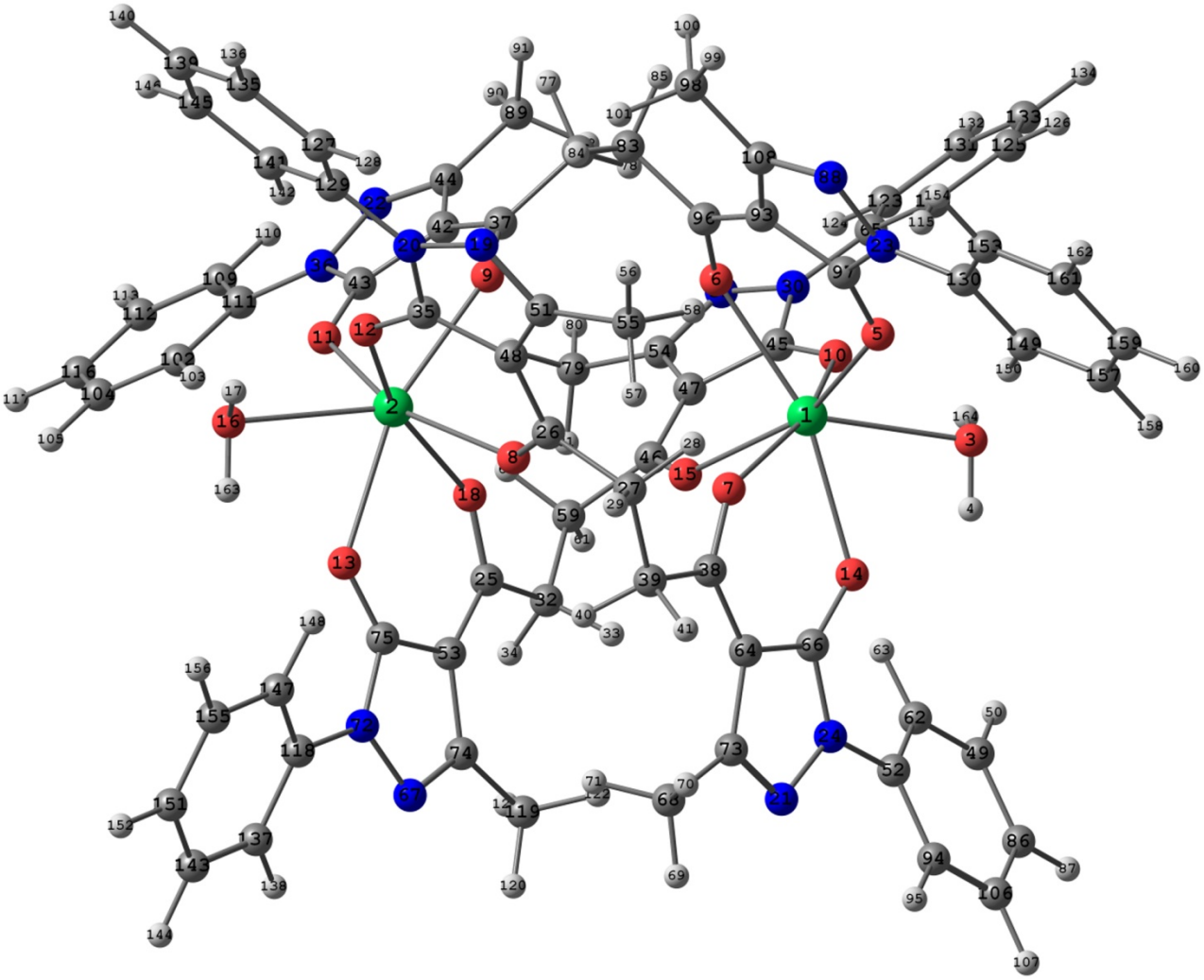

Figure S6. Equilibrium geometry configuration for $[Gd_2(Q_2Q_3)_3(H_2O)_2]$ (RI-DFT/PBE0).

Geometry optimization. Starting geometry for geometry optimization of $[Gd_2(Q_2Q_3)_3(H_2O)_2]$ has been based on the crystal structure of $[Tb_2(Q_2Q_3)_3(H_2O)_2]$. The crystallographically determined molecule has been modified by replace of terbium ion by gadolinium one and used without any other changes.

Table S5. Geometrical parameters for $[Gd_2(Q_2Q_3)_3(H_2O)_2]$ (RI-DFT/PBE0).

Atom	x	y	z
Gd	-3.013790000	-0.082280000	0.276750000
Gd	3.012650000	-0.078120000	-0.277180000
O	-5.493200000	0.199290000	0.155220000
H	-5.524300000	1.186680000	0.069110000
O	-3.506640000	-1.171160000	2.268380000
O	-1.624380000	-2.010420000	0.301440000
O	-1.483500000	1.078190000	1.650850000
O	1.704980000	0.706970000	1.555890000
O	1.623120000	-2.006650000	-0.304540000
O	-3.955620000	-1.067970000	-1.660730000
O	3.508960000	-1.166510000	-2.267950000
O	3.954650000	-1.067940000	1.658040000
O	3.718240000	2.190680000	-0.245940000
O	-3.720770000	2.186210000	0.247280000
O	-1.704940000	0.706160000	-1.554160000
O	5.491830000	0.206210000	-0.154760000
H	5.661460000	-0.180200000	0.740780000
O	1.481300000	1.082570000	-1.649950000
N	3.123890000	-2.147690000	4.905250000
N	3.878160000	-2.173240000	3.743890000
N	-2.571990000	5.477380000	0.739350000
N	2.111350000	-3.260220000	-4.726930000
N	-3.016800000	-2.324690000	4.272680000
N	-3.433020000	4.525770000	0.217920000
C	1.143280000	2.280810000	-1.900120000
C	1.521160000	0.405870000	2.775850000
C	0.516420000	1.230930000	3.573070000
H	-0.338920000	0.569100000	3.835220000
H	0.989870000	1.514020000	4.537930000
N	-3.877900000	-2.169740000	-3.748500000
N	-3.123340000	-2.141800000	-4.909600000
C	-0.012670000	2.502140000	-2.868260000
H	-0.840940000	2.994000000	-2.311490000
H	0.317280000	3.236180000	-3.634730000
C	3.402800000	-1.276870000	2.799340000
N	3.023060000	-2.319750000	-4.273310000
C	1.198070000	-2.825930000	-1.181960000
C	-1.146700000	2.276280000	1.903180000
C	0.008720000	2.497170000	2.872040000
H	0.836530000	2.991080000	2.316410000
H	-0.322430000	3.229550000	3.639600000
C	1.693560000	-2.819230000	-2.520810000
C	2.810820000	-2.002670000	-2.938470000
C	1.332780000	-3.575340000	-3.704150000
C	-3.403190000	-1.274880000	-2.802150000
C	-1.522220000	0.408560000	-2.775100000
C	-2.262790000	-0.636380000	-3.414240000
C	2.262340000	-0.639840000	3.412950000
C	-6.297860000	4.586980000	-2.189130000
H	-6.746760000	3.945590000	-2.965960000
C	2.174380000	-1.241450000	4.729670000
C	-4.579750000	4.951270000	-0.503280000
C	1.841630000	3.391150000	-1.330020000
C	-2.174210000	-1.235480000	-4.732030000
C	1.175100000	-1.026360000	5.829030000
H	1.420810000	-1.706130000	6.670750000

H	1.188130000	0.018170000	6.211740000
H	0.137320000	-1.250200000	5.496600000
C	-0.519390000	1.236730000	-3.571460000
H	0.336660000	0.576650000	-3.835740000
H	-0.994070000	1.521160000	-4.535320000
C	-5.165130000	4.132990000	-1.494420000
H	-4.717330000	3.158440000	-1.732350000
C	-1.846100000	3.386810000	1.334760000
C	-5.019430000	-3.015800000	-3.691980000
C	-3.053880000	3.236860000	0.557500000
N	2.565800000	5.481520000	-0.731800000
C	-0.531280000	5.605970000	2.054620000
H	-0.711550000	6.686060000	1.876030000
H	-0.487970000	5.437740000	3.153350000
H	0.467030000	5.349090000	1.635890000
N	3.428270000	4.529980000	-0.212770000
C	-1.633010000	4.820360000	1.404550000
C	1.627010000	4.824640000	-1.397310000
C	3.050260000	3.241300000	-0.554080000
C	0.166850000	-3.863150000	-0.750300000
H	0.550350000	-4.865740000	-1.040720000
H	-0.756840000	-3.704810000	-1.348260000
C	-1.174490000	-1.018120000	-5.830540000
H	-1.419280000	-1.696870000	-6.673370000
H	-1.188260000	0.026920000	-6.211870000
H	-0.136710000	-1.241440000	-5.497850000
C	-0.164450000	-3.864570000	0.744990000
H	0.759070000	-3.707510000	1.343480000
H	-0.548050000	-4.867760000	1.033330000
C	-6.847530000	5.851050000	-1.916900000
H	-7.735230000	6.202020000	-2.468010000
N	-2.103460000	-3.264460000	4.724630000
C	0.238170000	-4.580500000	-3.917620000
H	0.267600000	-4.920220000	-4.973270000
H	0.353990000	-5.471680000	-3.262180000
H	-0.768380000	-4.149190000	-3.721030000
C	-1.688990000	-2.821930000	2.518150000
C	-5.120460000	6.227170000	-0.235200000
H	-4.634970000	6.857270000	0.523550000
C	-1.196070000	-2.828490000	1.178390000
C	-2.806760000	-2.006880000	2.937620000
C	-0.229820000	-4.582180000	3.912280000
H	-0.258760000	-4.923870000	4.967310000
H	-0.344250000	-5.472260000	3.255150000
H	0.776090000	-4.148910000	3.716690000
C	5.014710000	-0.930230000	-4.765220000
H	5.075270000	-0.627110000	-3.712610000
C	5.944980000	-0.454850000	-5.703480000
H	6.738030000	0.232950000	-5.365530000
C	-6.247400000	6.668660000	-0.942770000
H	-6.663250000	7.666690000	-0.726090000
C	-1.325830000	-3.578160000	3.700640000
C	3.924740000	-2.213980000	-6.537340000
H	3.130610000	-2.908850000	-6.842070000
C	3.992520000	-1.812890000	-5.183380000
C	4.864110000	-1.729300000	-7.457950000
H	4.799160000	-2.050780000	-8.510980000
C	-5.607870000	-3.384160000	-2.461350000
H	-5.178600000	-3.021790000	-1.518510000

C	5.878990000	-0.845380000	-7.051100000
H	6.614850000	-0.466780000	-7.779330000
C	4.575060000	4.955340000	0.508370000
C	0.523830000	5.610220000	-2.044920000
H	0.702830000	6.690150000	-1.864070000
H	0.480000000	5.444390000	-3.144000000
H	-0.473880000	5.351170000	-1.626090000
C	-5.558030000	-3.507720000	-4.901850000
H	-5.075130000	-3.224300000	-5.847280000
C	-6.734270000	-4.222710000	-2.455000000
H	-7.184460000	-4.506250000	-1.489130000
C	5.557810000	-3.513930000	4.894500000
H	5.074040000	-3.233510000	5.840360000
C	5.019900000	-3.018870000	3.685610000
C	-3.985650000	-1.819450000	5.184330000
C	-6.679500000	-4.348160000	-4.876020000
H	-7.091120000	-4.725860000	-5.826870000
C	-7.278730000	-4.707440000	-3.655710000
H	-8.162300000	-5.366300000	-3.640810000
C	6.679760000	-4.353670000	4.867100000
H	7.090780000	-4.734010000	5.817150000
C	5.115200000	6.231590000	0.241020000
H	4.629480000	6.861950000	-0.517360000
C	7.280080000	-4.709110000	3.646180000
H	8.164040000	-5.367420000	3.630060000
C	5.609330000	-3.383420000	2.454340000
H	5.180480000	-3.018650000	1.512250000
C	6.241930000	6.673120000	0.948880000
H	6.657410000	7.671440000	0.732810000
C	6.736170000	-4.221370000	2.446430000
H	7.187190000	-4.501950000	1.480080000
C	5.160760000	4.136620000	1.498910000
H	4.713400000	3.161720000	1.736290000
C	-5.007350000	-0.934920000	4.768830000
H	-5.068270000	-0.629320000	3.716960000
C	6.842350000	5.855150000	1.922540000
H	7.729840000	6.206200000	2.473960000
C	-3.917590000	-2.223930000	6.537290000
H	-3.123800000	-2.920090000	6.839980000
C	6.293280000	4.590640000	2.193940000
H	6.742400000	3.949000000	2.970450000
C	-5.936770000	-0.461100000	5.708740000
H	-6.729440000	0.228150000	5.372860000
C	-5.870380000	-0.854920000	7.055380000
H	-6.605440000	-0.477370000	7.784960000
C	-4.856060000	-1.740680000	7.459560000
H	-4.790880000	-2.064850000	8.511750000
H	5.521010000	1.193510000	-0.066640000
H	-5.661890000	-0.185600000	-0.741210000

Table S6. Geometrical parameters of equilibrium geometry configuration of $[Gd_2(Q_2Q_3)_3(H_2O)_2]$ (RI-DFT/PBE0).

R(1-3)	2.498	R(32-34)	1.111
R(1-5)	2.323	R(32-59)	1.534
R(1-6)	2.377	R(35-48)	1.443
R(1-7)	2.361	R(36-43)	1.388
R(1-10)	2.369	R(36-111)	1.423
R(1-14)	2.376	R(37-42)	1.428
R(1-15)	2.385	R(37-76)	1.525
R(2-8)	2.385	R(38-39)	1.524
R(2-9)	2.377	R(38-64)	1.430
R(2-11)	2.323	R(39-40)	1.113
R(2-12)	2.369	R(39-41)	1.111
R(2-13)	2.376	R(42-43)	1.446
R(2-16)	2.498	R(42-44)	1.450
R(2-18)	2.362	R(44-89)	1.501
R(3-4)	0.992	R(45-47)	1.443
R(3-164)	0.990	R(46-47)	1.431
R(5-97)	1.279	R(46-59)	1.525
R(6-96)	1.273	R(47-54)	1.450
R(7-38)	1.270	R(48-51)	1.450
R(8-26)	1.270	R(49-50)	1.103
R(9-37)	1.273	R(49-62)	1.404
R(10-45)	1.285	R(49-86)	1.405
R(11-43)	1.279	R(51-55)	1.501
R(12-35)	1.285	R(52-62)	1.412
R(13-75)	1.283	R(52-94)	1.411
R(14-66)	1.283	R(53-74)	1.451
R(15-46)	1.270	R(53-75)	1.444
R(16-17)	0.990	R(54-79)	1.501
R(16-163)	0.992	R(55-56)	1.109
R(18-25)	1.270	R(55-57)	1.113
R(19-20)	1.385	R(55-58)	1.112
R(19-51)	1.324	R(59-60)	1.113
R(20-35)	1.386	R(59-61)	1.111
R(20-129)	1.422	R(62-63)	1.099
R(21-24)	1.385	R(64-66)	1.444
R(21-73)	1.325	R(64-73)	1.451
R(22-36)	1.386	R(65-114)	1.413
R(22-44)	1.323	R(65-123)	1.413
R(23-88)	1.386	R(67-72)	1.385
R(23-97)	1.388	R(67-74)	1.325
R(23-130)	1.423	R(68-69)	1.109
R(24-52)	1.420	R(68-70)	1.112
R(24-66)	1.386	R(68-71)	1.113
R(25-32)	1.524	R(68-73)	1.501
R(25-53)	1.430	R(72-75)	1.386
R(26-27)	1.525	R(72-118)	1.420
R(26-48)	1.431	R(74-119)	1.501
R(27-28)	1.113	R(76-77)	1.112
R(27-29)	1.111	R(76-78)	1.112
R(27-39)	1.534	R(76-83)	1.532
R(30-31)	1.385	R(79-80)	1.109
R(30-45)	1.386	R(79-81)	1.113
R(30-65)	1.422	R(79-82)	1.112
R(31-54)	1.324	R(83-84)	1.112
R(32-33)	1.113	R(83-85)	1.112

R(83-96)	1.525	R(147-148)	1.099
R(86-87)	1.102	R(147-155)	1.404
R(86-106)	1.406	R(149-150)	1.097
R(88-108)	1.324	R(149-157)	1.404
R(89-90)	1.109	R(151-152)	1.102
R(89-91)	1.112	R(151-155)	1.405
R(89-92)	1.113	R(153-154)	1.098
R(93-96)	1.428	R(153-161)	1.402
R(93-97)	1.446	R(155-156)	1.103
R(93-108)	1.450	R(157-158)	1.103
R(94-95)	1.099	R(157-159)	1.405
R(94-106)	1.402	R(159-160)	1.102
R(98-99)	1.109	R(159-161)	1.406
R(98-100)	1.112	R(161-162)	1.103
R(98-101)	1.113	A(3-1-5)	83.3
R(98-108)	1.501	A(3-1-6)	132.2
R(102-103)	1.097	A(3-1-7)	128.0
R(102-104)	1.404	A(3-1-10)	67.2
R(102-111)	1.414	A(3-1-14)	66.2
R(104-105)	1.103	A(3-1-15)	118.0
R(104-116)	1.405	A(1-3-4)	98.5
R(106-107)	1.103	A(1-3-164)	99.7
R(109-110)	1.098	A(5-1-6)	74.6
R(109-111)	1.414	A(5-1-7)	82.5
R(109-112)	1.402	A(5-1-10)	115.0
R(112-113)	1.103	A(5-1-14)	113.3
R(112-116)	1.406	A(5-1-15)	158.4
R(114-115)	1.098	A(1-5-97)	129.7
R(114-125)	1.404	A(6-1-7)	90.8
R(116-117)	1.102	A(6-1-10)	84.5
R(118-137)	1.411	A(6-1-14)	161.5
R(118-147)	1.412	A(6-1-15)	87.4
R(119-120)	1.110	A(1-6-96)	136.5
R(119-121)	1.112	A(7-1-10)	159.7
R(119-122)	1.113	A(7-1-14)	74.4
R(123-124)	1.099	A(7-1-15)	85.9
R(123-131)	1.402	A(1-7-38)	138.7
R(125-126)	1.103	A(10-1-14)	105.6
R(125-133)	1.405	A(10-1-15)	74.2
R(127-128)	1.099	A(1-10-45)	128.5
R(127-129)	1.413	A(14-1-15)	80.7
R(127-135)	1.402	A(1-14-66)	128.6
R(129-141)	1.413	A(1-15-46)	137.7
R(130-149)	1.414	A(8-2-9)	87.4
R(130-153)	1.414	A(8-2-11)	158.5
R(131-132)	1.103	A(8-2-12)	74.2
R(131-133)	1.406	A(8-2-13)	80.7
R(133-134)	1.102	A(8-2-16)	118.0
R(135-136)	1.103	A(8-2-18)	86.0
R(135-139)	1.406	A(2-8-26)	137.7
R(137-138)	1.099	A(9-2-11)	74.6
R(137-143)	1.402	A(9-2-12)	84.4
R(139-140)	1.102	A(9-2-13)	161.5
R(139-145)	1.405	A(9-2-16)	132.3
R(141-142)	1.097	A(9-2-18)	90.7
R(141-145)	1.404	A(2-9-37)	136.5
R(143-144)	1.103	A(11-2-12)	114.8
R(143-151)	1.406	A(11-2-13)	113.3
R(145-146)	1.103	A(11-2-16)	83.3

A(11-2-18)	82.6	A(88-23-130)	118.7
A(2-11-43)	129.7	A(23-88-108)	107.2
A(12-2-13)	105.7	A(97-23-130)	129.6
A(12-2-16)	67.2	A(23-97-93)	105.5
A(12-2-18)	159.7	A(23-130-149)	121.7
A(2-12-35)	128.5	A(23-130-153)	118.6
A(13-2-16)	66.2	A(52-24-66)	128.6
A(13-2-18)	74.4	A(24-52-62)	121.2
A(2-13-75)	128.6	A(24-52-94)	118.9
A(16-2-18)	128.0	A(24-66-64)	105.3
A(2-16-17)	99.8	A(32-25-53)	120.7
A(2-16-163)	98.4	A(25-32-33)	108.1
A(2-18-25)	138.7	A(25-32-34)	108.0
A(4-3-164)	107.6	A(25-32-59)	115.0
A(5-97-23)	124.7	A(25-53-74)	132.6
A(5-97-93)	129.8	A(25-53-75)	122.8
A(6-96-83)	117.9	A(27-26-48)	120.2
A(6-96-93)	121.8	A(26-27-28)	107.9
A(7-38-39)	117.7	A(26-27-29)	108.1
A(7-38-64)	121.6	A(26-27-39)	115.2
A(8-26-27)	118.0	A(26-48-35)	122.8
A(8-26-48)	121.7	A(26-48-51)	132.5
A(9-37-42)	121.8	A(28-27-29)	105.9
A(9-37-76)	117.9	A(28-27-39)	110.1
A(10-45-30)	124.3	A(29-27-39)	109.1
A(10-45-47)	130.2	A(27-39-38)	115.0
A(11-43-36)	124.7	A(27-39-40)	110.4
A(11-43-42)	129.8	A(27-39-41)	109.1
A(12-35-20)	124.3	A(31-30-45)	111.9
A(12-35-48)	130.2	A(31-30-65)	118.9
A(13-75-53)	130.5	A(30-31-54)	107.0
A(13-75-72)	124.1	A(45-30-65)	129.2
A(14-66-24)	124.1	A(30-45-47)	105.5
A(14-66-64)	130.6	A(30-65-114)	121.6
A(15-46-47)	121.7	A(30-65-123)	118.6
A(15-46-59)	118.0	A(31-54-47)	111.1
A(17-16-163)	107.6	A(31-54-79)	118.6
A(18-25-32)	117.7	A(33-32-34)	105.9
A(18-25-53)	121.6	A(33-32-59)	110.4
A(20-19-51)	107.0	A(34-32-59)	109.1
A(19-20-35)	111.9	A(32-59-46)	115.2
A(19-20-129)	118.9	A(32-59-60)	110.1
A(19-51-48)	111.1	A(32-59-61)	109.1
A(19-51-55)	118.6	A(35-48-51)	104.5
A(35-20-129)	129.2	A(43-36-111)	129.6
A(20-35-48)	105.5	A(36-43-42)	105.5
A(20-129-127)	118.6	A(36-111-102)	121.7
A(20-129-141)	121.6	A(36-111-109)	118.6
A(24-21-73)	106.8	A(42-37-76)	120.2
A(21-24-52)	119.2	A(37-42-43)	122.8
A(21-24-66)	112.1	A(37-42-44)	132.6
A(21-73-64)	111.2	A(37-76-77)	107.8
A(21-73-68)	118.6	A(37-76-78)	108.2
A(36-22-44)	107.2	A(37-76-83)	115.0
A(22-36-43)	111.7	A(39-38-64)	120.7
A(22-36-111)	118.7	A(38-39-40)	108.1
A(22-44-42)	111.1	A(38-39-41)	108.0
A(22-44-89)	118.6	A(38-64-66)	122.8
A(88-23-97)	111.7	A(38-64-73)	132.5

A(40-39-41)	105.9	A(74-119-120)	108.7
A(43-42-44)	104.5	A(74-119-121)	112.2
A(42-44-89)	130.3	A(74-119-122)	112.0
A(44-89-90)	108.7	A(77-76-78)	105.9
A(44-89-91)	112.1	A(77-76-83)	109.2
A(44-89-92)	112.0	A(78-76-83)	110.2
A(45-47-46)	122.8	A(76-83-84)	110.2
A(45-47-54)	104.5	A(76-83-85)	109.2
A(47-46-59)	120.2	A(76-83-96)	115.0
A(46-47-54)	132.5	A(80-79-81)	108.2
A(46-59-60)	107.9	A(80-79-82)	108.1
A(46-59-61)	108.1	A(81-79-82)	107.6
A(47-54-79)	130.2	A(84-83-85)	105.9
A(48-51-55)	130.2	A(84-83-96)	108.2
A(50-49-62)	119.3	A(85-83-96)	107.8
A(50-49-86)	120.0	A(83-96-93)	120.2
A(62-49-86)	120.7	A(87-86-106)	120.3
A(49-62-52)	119.6	A(86-106-94)	120.6
A(49-62-63)	120.6	A(86-106-107)	120.1
A(49-86-87)	120.3	A(88-108-93)	111.1
A(49-86-106)	119.4	A(88-108-98)	118.6
A(51-55-56)	108.7	A(90-89-91)	108.2
A(51-55-57)	112.3	A(90-89-92)	108.1
A(51-55-58)	111.9	A(91-89-92)	107.5
A(62-52-94)	119.9	A(96-93-97)	122.8
A(52-62-63)	119.8	A(96-93-108)	132.6
A(52-94-95)	118.7	A(97-93-108)	104.5
A(52-94-106)	119.8	A(93-108-98)	130.3
A(74-53-75)	104.6	A(95-94-106)	121.5
A(53-74-67)	111.2	A(94-106-107)	119.3
A(53-74-119)	130.2	A(99-98-100)	108.2
A(53-75-72)	105.3	A(99-98-101)	108.1
A(54-79-80)	108.7	A(99-98-108)	108.7
A(54-79-81)	112.2	A(100-98-101)	107.5
A(54-79-82)	111.9	A(100-98-108)	112.1
A(56-55-57)	108.2	A(101-98-108)	112.0
A(56-55-58)	108.1	A(103-102-104)	120.7
A(57-55-58)	107.6	A(103-102-111)	119.7
A(60-59-61)	105.9	A(104-102-111)	119.5
A(66-64-73)	104.6	A(102-104-105)	118.9
A(64-73-68)	130.2	A(102-104-116)	121.1
A(114-65-123)	119.8	A(102-111-109)	119.7
A(65-114-115)	120.0	A(105-104-116)	120.1
A(65-114-125)	119.6	A(104-116-112)	119.1
A(65-123-124)	118.7	A(104-116-117)	120.5
A(65-123-131)	119.9	A(110-109-111)	118.7
A(72-67-74)	106.8	A(110-109-112)	121.4
A(67-72-75)	112.1	A(111-109-112)	119.9
A(67-72-118)	119.2	A(109-112-113)	119.1
A(67-74-119)	118.5	A(109-112-116)	120.7
A(69-68-70)	108.2	A(113-112-116)	120.1
A(69-68-71)	108.1	A(112-116-117)	120.4
A(69-68-73)	108.7	A(115-114-125)	120.5
A(70-68-71)	107.6	A(114-125-126)	119.0
A(70-68-73)	112.2	A(114-125-133)	120.9
A(71-68-73)	112.0	A(137-118-147)	119.9
A(75-72-118)	128.6	A(118-137-138)	118.7
A(72-118-137)	118.9	A(118-137-143)	119.8
A(72-118-147)	121.2	A(118-147-148)	119.8

A(118-147-155)	119.6	A(138-137-143)	121.5
A(120-119-121)	108.2	A(137-143-144)	119.3
A(120-119-122)	108.1	A(137-143-151)	120.6
A(121-119-122)	107.6	A(140-139-145)	120.4
A(124-123-131)	121.5	A(139-145-141)	120.9
A(123-131-132)	119.2	A(139-145-146)	120.1
A(123-131-133)	120.7	A(142-141-145)	120.5
A(126-125-133)	120.1	A(141-145-146)	119.0
A(125-133-131)	119.2	A(144-143-151)	120.1
A(125-133-134)	120.4	A(143-151-152)	120.3
A(128-127-129)	118.7	A(143-151-155)	119.4
A(128-127-135)	121.5	A(148-147-155)	120.6
A(129-127-135)	119.9	A(147-155-151)	120.7
A(127-129-141)	119.8	A(147-155-156)	119.3
A(127-135-136)	119.2	A(150-149-157)	120.7
A(127-135-139)	120.7	A(149-157-158)	118.9
A(129-141-142)	120.0	A(149-157-159)	121.1
A(129-141-145)	119.6	A(152-151-155)	120.3
A(149-130-153)	119.7	A(151-155-156)	120.0
A(130-149-150)	119.7	A(154-153-161)	121.4
A(130-149-157)	119.5	A(153-161-159)	120.7
A(130-153-154)	118.7	A(153-161-162)	119.1
A(130-153-161)	119.9	A(158-157-159)	120.1
A(132-131-133)	120.1	A(157-159-160)	120.5
A(131-133-134)	120.4	A(157-159-161)	119.1
A(136-135-139)	120.1	A(160-159-161)	120.4
A(135-139-140)	120.4	A(159-161-162)	120.1
A(135-139-145)	119.2		

VIII. Theoretical modeling of tetrahydrated helical complex of Gd, $[Gd_2(Q_2Q_3)_3(H_2O)_4]$

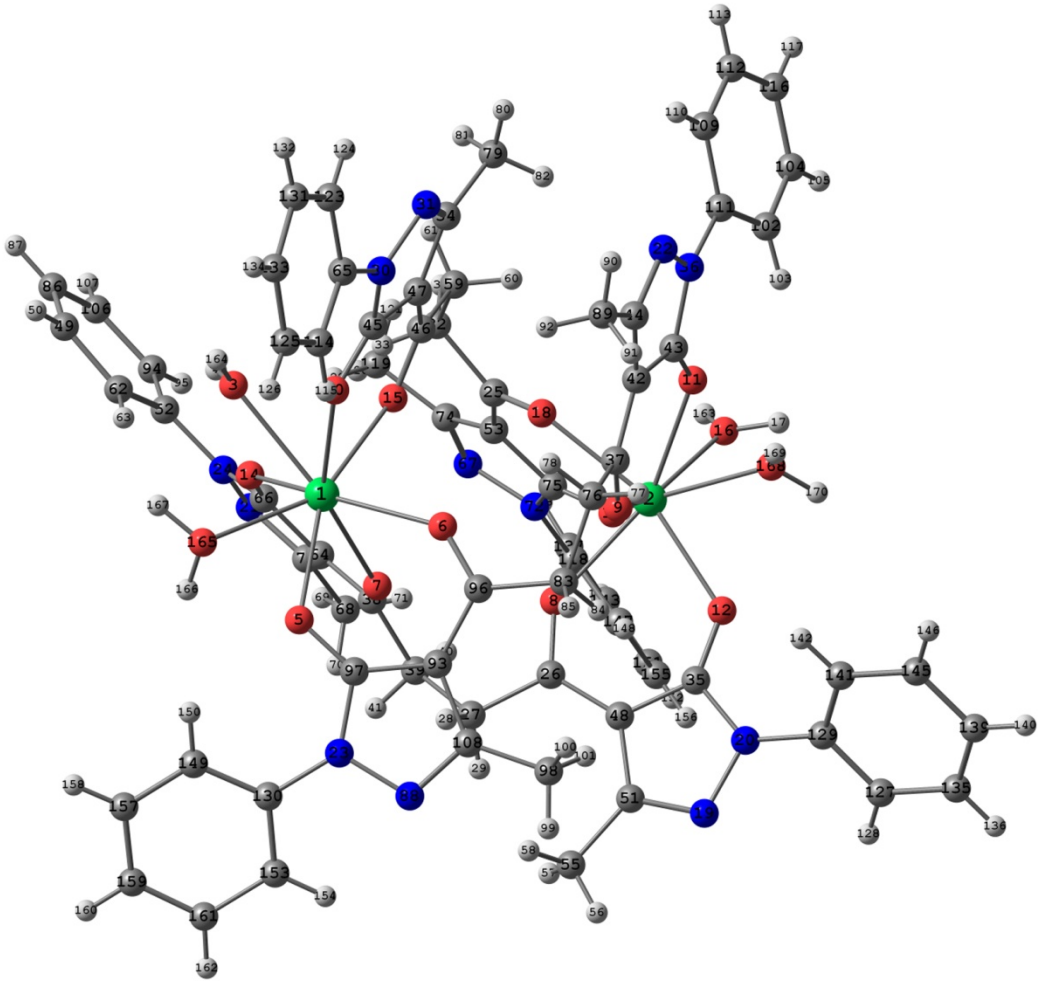

Figure S7. Starting geometry configuration for $[Gd_2(Q_2Q_3)_3(H_2O)_4]$ (RI-DFT/PBE0).

Geometry optimization. Starting geometry of the tetrahydrated helical complex of gadolinium was constructed based on crystal structure of complex $[Tb_2(Q_2Q_3)_3(H_2O)_2]$. Terbium ion has been replaced by gadolinium one and additional water molecule per metal center was added. The distance between oxygen in the second water molecule and gadolinium ion has been taken the same as it found in the crystal structure of $[Tb_2(Q_2Q_3)_3(H_2O)_2]$. The angle between the first and the second water molecules was equal to 72^o. For this reason, position of the first water molecule was slightly shifted in comparison with original crystallographically determined in $[Tb_2(Q_2Q_3)_3(H_2O)_2]$. The final starting geometry of $[Gd_2(Q_2Q_3)_3(H_2O)_4]$ is presented in Figure S7.

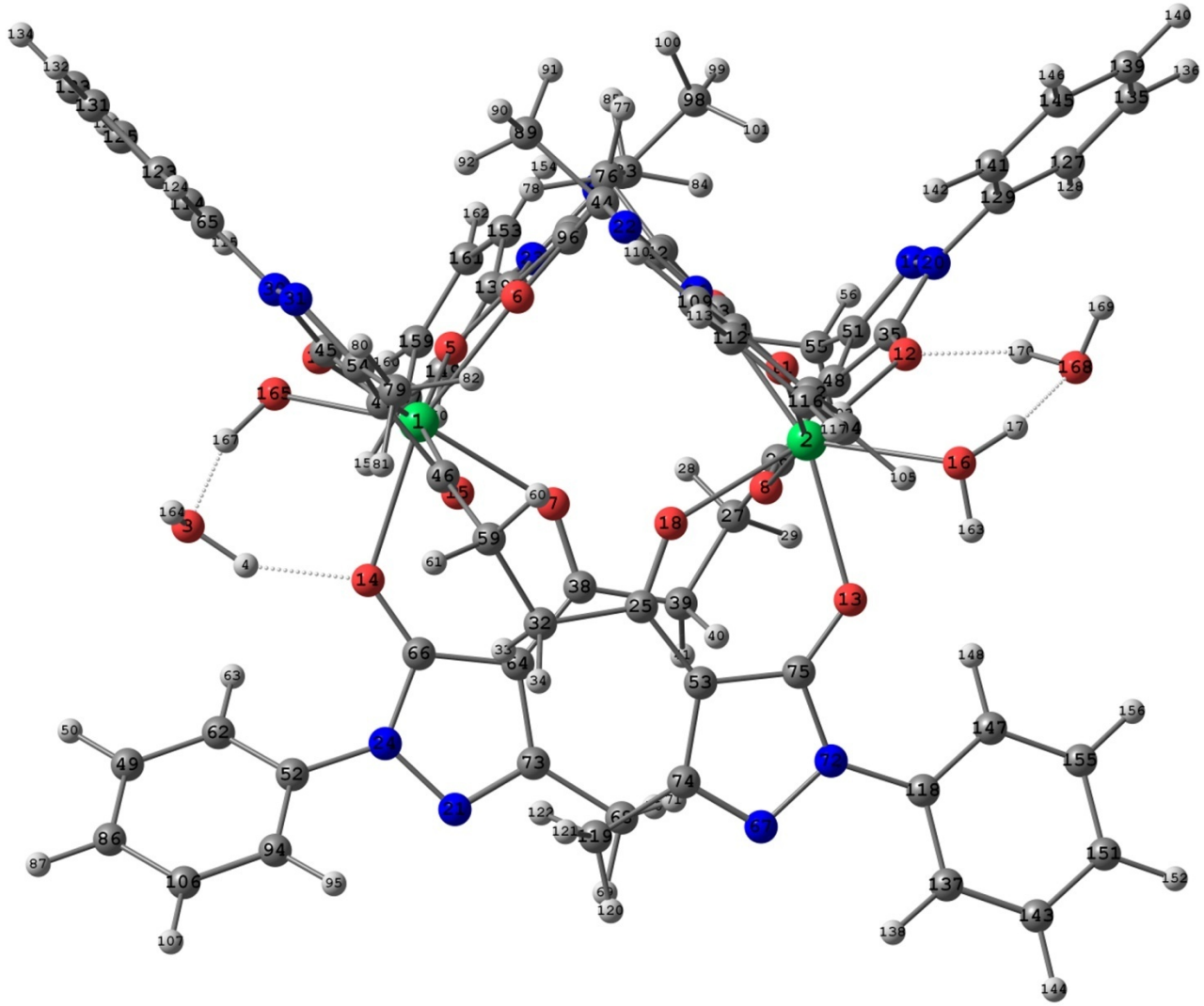

Figure S8. Equilibrium geometry configuration for $[Gd_2(Q_2Q_3)_3(H_2O)_4]$ (RI-DFT/PBE0).

Table S7. Cartesian coordinates of equilibrium geometry configuration of $[Gd_2(Q_2Q_3)_3(H_2O)_4]$ (RI-DFT/PBE0).

Atom	x	y	z
Gd	-0.167500000	-0.163830000	-3.087200000
Gd	0.202990000	0.069900000	3.180100000
O	1.465590000	1.030690000	-6.124300000
H	1.246800000	1.650290000	-5.364050000
O	-2.396090000	-0.819940000	-3.504120000
O	-0.595600000	-1.908230000	-1.558600000
O	-1.369380000	1.276420000	-1.627830000
O	-1.426960000	1.070850000	1.726700000
O	-0.037960000	-1.859100000	1.757240000
O	1.656040000	-1.469400000	-3.742530000
O	1.982790000	-1.332560000	3.692330000
O	-1.935600000	-0.774840000	3.871490000
O	0.427780000	2.361380000	3.754650000
O	0.215470000	2.077790000	-3.927550000
O	1.703190000	0.517420000	-1.711680000
O	0.263670000	0.400970000	5.579450000

H	-0.508140000	0.028470000	6.157420000
O	1.756860000	0.971530000	1.634580000
N	-5.151270000	-1.510200000	2.641320000
N	-4.063200000	-1.703170000	3.474780000
N	0.228310000	5.442980000	-2.856850000
N	4.103450000	-3.815080000	2.383240000
N	-4.533120000	-1.718490000	-3.073710000
N	0.529690000	4.413260000	-3.731830000
C	2.137940000	2.114910000	1.232140000
C	-2.637480000	0.903710000	1.398780000
C	-3.238710000	1.832830000	0.350140000
H	-3.611030000	1.210060000	-0.492300000
H	-4.139410000	2.304720000	0.802270000
N	3.563950000	-2.833530000	-3.468020000
N	4.674600000	-2.900800000	-2.642160000
C	3.112590000	2.169750000	0.061820000
H	2.590340000	2.656120000	-0.791980000
H	3.947480000	2.847980000	0.340430000
C	-3.013140000	-0.855310000	3.166740000
N	3.787710000	-2.795950000	3.267500000
C	0.700240000	-2.818870000	1.367310000
C	-1.412130000	2.508790000	-1.335530000
C	-2.301460000	2.929030000	-0.169870000
H	-1.641140000	3.287090000	0.651600000
H	-2.903010000	3.807140000	-0.487980000
C	2.010210000	-3.027430000	1.898700000
C	2.526580000	-2.271470000	3.015600000
C	3.062560000	-3.972520000	1.580730000
C	2.734310000	-1.773820000	-3.124570000
C	2.843970000	0.053330000	-1.397310000
C	3.374960000	-1.126820000	-2.006350000
C	-3.450960000	-0.099640000	2.024920000
C	1.799010000	4.455990000	-7.250520000
H	1.554360000	4.004480000	-8.225620000
C	-4.805230000	-0.560630000	1.781840000
C	1.316540000	4.707880000	-4.879570000
C	1.698050000	3.320740000	1.861270000
C	4.583840000	-1.896310000	-1.784040000
C	-5.792450000	-0.153250000	0.727690000
H	-6.727800000	-0.731330000	0.872670000
H	-6.037550000	0.930340000	0.781160000
H	-5.417710000	-0.364870000	-0.297640000
C	3.679450000	0.814030000	-0.371520000
H	3.815930000	0.154910000	0.514020000
H	4.693870000	0.960440000	-0.801970000
C	1.004890000	4.147700000	-6.133750000
H	0.129150000	3.491940000	-6.240930000
C	-0.687310000	3.488330000	-2.087490000
C	3.420340000	-3.795100000	-4.507020000
C	0.029430000	3.193880000	-3.307770000
N	1.340640000	5.502960000	2.460500000
C	-1.006530000	5.819280000	-0.800150000
H	-0.617560000	6.841880000	-0.985260000
H	-2.117530000	5.874660000	-0.775850000
H	-0.664540000	5.495140000	0.207220000
N	0.685860000	4.670820000	3.353300000
C	-0.510730000	4.915550000	-1.891770000
C	1.946670000	4.721680000	1.579060000
C	0.879170000	3.329760000	3.050980000

C	0.134270000	-3.798070000	0.342220000
H	0.269280000	-4.824690000	0.747460000
H	0.766050000	-3.744330000	-0.571250000
C	5.656950000	-1.742330000	-0.745720000
H	6.409330000	-2.544750000	-0.890700000
H	6.176070000	-0.761170000	-0.818480000
H	5.251250000	-1.833280000	0.285880000
C	-1.338850000	-3.592890000	-0.024520000
H	-1.919990000	-3.278020000	0.870510000
H	-1.773580000	-4.563940000	-0.346150000
C	2.883360000	5.340270000	-7.130650000
H	3.499600000	5.585000000	-8.011270000
N	-5.122050000	-2.620980000	-2.202090000
C	3.138900000	-5.016340000	0.504600000
H	4.121640000	-5.526490000	0.572390000
H	2.340320000	-5.784040000	0.606660000
H	3.050340000	-4.573070000	-0.511720000
C	-2.898950000	-2.419590000	-1.686050000
C	2.395670000	5.608440000	-4.756710000
H	2.600890000	6.062350000	-3.776140000
C	-1.592110000	-2.577140000	-1.132880000
C	-3.176100000	-1.560060000	-2.816330000
C	-4.545530000	-4.023820000	-0.306440000
H	-5.625480000	-4.260020000	-0.401010000
H	-3.972560000	-4.973770000	-0.386450000
H	-4.373590000	-3.608450000	0.710990000
C	4.464740000	-1.439060000	5.228090000
H	3.485510000	-0.944300000	5.235290000
C	5.445280000	-1.107170000	6.177280000
H	5.215840000	-0.336240000	6.931740000
C	3.170340000	5.922490000	-5.882070000
H	4.011410000	6.628420000	-5.781360000
C	-4.173370000	-3.045100000	-1.382410000
C	6.002200000	-3.070140000	4.252060000
H	6.198960000	-3.839190000	3.493010000
C	4.743680000	-2.425570000	4.254070000
C	6.966910000	-2.724860000	5.208660000
H	7.944330000	-3.235710000	5.193960000
C	2.266140000	-3.842150000	-5.322650000
H	1.456030000	-3.119860000	-5.162230000
C	6.698870000	-1.741130000	6.176970000
H	7.461220000	-1.472760000	6.926620000
C	-0.018980000	5.248690000	4.442660000
C	2.727290000	5.366140000	0.470380000
H	2.657930000	6.467900000	0.581050000
H	3.802990000	5.082320000	0.497230000
H	2.333050000	5.090670000	-0.532770000
C	4.463110000	-4.726990000	-4.715480000
H	5.350800000	-4.677600000	-4.070430000
C	2.171240000	-4.815060000	-6.330940000
H	1.265350000	-4.842250000	-6.959420000
C	-5.415360000	-2.904460000	5.112140000
H	-6.296670000	-2.380370000	4.715580000
C	-4.154020000	-2.639220000	4.538250000
C	-5.325010000	-1.144000000	-4.103460000
C	4.347900000	-5.690400000	-5.727040000
H	5.168820000	-6.411410000	-5.878060000
C	3.203860000	-5.743200000	-6.542650000
H	3.118050000	-6.502910000	-7.336820000

C	-5.523160000	-3.831800000	6.158620000
H	-6.512500000	-4.032780000	6.601850000
C	0.291350000	6.571230000	4.829340000
H	1.069370000	7.113640000	4.274610000
C	-4.384480000	-4.498860000	6.644920000
H	-4.474950000	-5.225300000	7.468750000
C	-3.008670000	-3.323730000	5.004190000
H	-2.034910000	-3.156110000	4.521660000
C	-0.397850000	7.166970000	5.895060000
H	-0.146340000	8.199840000	6.188480000
C	-3.132060000	-4.243600000	6.059330000
H	-2.236780000	-4.783760000	6.410300000
C	-1.032530000	4.538160000	5.124590000
H	-1.291790000	3.519900000	4.807010000
C	-4.903960000	0.006810000	-4.807830000
H	-3.944620000	0.476680000	-4.556170000
C	-1.396930000	6.460100000	6.587990000
H	-1.933330000	6.932220000	7.427190000
C	-6.571540000	-1.734650000	-4.410890000
H	-6.889290000	-2.619510000	-3.842230000
C	-1.708480000	5.147950000	6.194040000
H	-2.498820000	4.585650000	6.718620000
C	-5.722680000	0.541950000	-5.815360000
H	-5.386480000	1.442650000	-6.356190000
C	-6.958670000	-0.046640000	-6.130250000
H	-7.594550000	0.381200000	-6.922500000
C	-7.376670000	-1.184180000	-5.417420000
H	-8.346510000	-1.655800000	-5.648410000
H	0.326180000	1.375720000	5.709120000
H	2.354160000	0.654690000	-5.942590000
O	-0.444680000	-0.537930000	-5.458920000
H	-1.326450000	-0.426520000	-5.872250000
H	0.278810000	0.002600000	-5.955720000
O	-1.899040000	-0.574910000	6.556100000
H	-1.951790000	-1.440620000	7.016590000
H	-2.151400000	-0.763640000	5.600120000

Table S8. Geometrical parameters of equilibrium geometry configuration of $[Gd_2(Q_2Q_3)_3(H_2O)_4]$ (RI-DFT/PBE0).

R(1-5)	2.360	R(6-96)	1.273
R(1-6)	2.359	R(7-38)	1.267
R(1-7)	2.377	R(8-26)	1.265
R(1-10)	2.337	R(9-37)	1.272
R(1-14)	2.424	R(10-45)	1.280
R(1-15)	2.420	R(11-43)	1.279
R(1-165)	2.417	R(12-35)	1.290
R(2-8)	2.402	R(13-75)	1.279
R(2-9)	2.409	R(14-66)	1.290
R(2-11)	2.323	R(15-46)	1.271
R(2-12)	2.401	R(16-17)	1.034
R(2-13)	2.373	R(16-163)	0.985
R(2-16)	2.423	R(18-25)	1.271
R(2-18)	2.370	R(19-20)	1.384
R(3-4)	1.005	R(19-51)	1.327
R(3-164)	0.982	R(20-35)	1.384
R(5-97)	1.276	R(20-129)	1.420

R(21-24)	1.384	R(67-72)	1.385
R(21-73)	1.325	R(67-74)	1.325
R(22-36)	1.386	R(68-69)	1.110
R(22-44)	1.324	R(68-70)	1.113
R(23-88)	1.386	R(68-71)	1.112
R(23-97)	1.390	R(68-73)	1.501
R(23-130)	1.420	R(72-75)	1.388
R(24-52)	1.422	R(72-118)	1.420
R(24-66)	1.385	R(74-119)	1.501
R(25-32)	1.524	R(76-77)	1.112
R(25-53)	1.429	R(76-78)	1.112
R(26-27)	1.525	R(76-83)	1.532
R(26-48)	1.435	R(79-80)	1.109
R(27-28)	1.112	R(79-81)	1.112
R(27-29)	1.113	R(79-82)	1.112
R(27-39)	1.533	R(83-84)	1.113
R(30-31)	1.386	R(83-85)	1.111
R(30-45)	1.389	R(83-96)	1.525
R(30-65)	1.423	R(86-87)	1.102
R(31-54)	1.324	R(86-106)	1.407
R(32-33)	1.113	R(88-108)	1.324
R(32-34)	1.111	R(89-90)	1.109
R(32-59)	1.532	R(89-91)	1.112
R(35-48)	1.438	R(89-92)	1.112
R(36-43)	1.389	R(93-96)	1.428
R(36-111)	1.423	R(93-97)	1.447
R(37-42)	1.429	R(93-108)	1.452
R(37-76)	1.526	R(94-95)	1.100
R(38-39)	1.525	R(94-106)	1.402
R(38-64)	1.432	R(98-99)	1.110
R(39-40)	1.113	R(98-100)	1.112
R(39-41)	1.111	R(98-101)	1.112
R(42-43)	1.444	R(98-108)	1.501
R(42-44)	1.450	R(102-103)	1.097
R(44-89)	1.501	R(102-104)	1.404
R(45-47)	1.442	R(102-111)	1.414
R(46-47)	1.430	R(104-105)	1.103
R(46-59)	1.526	R(104-116)	1.405
R(47-54)	1.450	R(106-107)	1.103
R(48-51)	1.451	R(109-110)	1.098
R(49-50)	1.102	R(109-111)	1.414
R(49-62)	1.405	R(109-112)	1.402
R(49-86)	1.404	R(112-113)	1.103
R(51-55)	1.501	R(112-116)	1.406
R(52-62)	1.409	R(114-115)	1.097
R(52-94)	1.411	R(114-125)	1.404
R(53-74)	1.451	R(116-117)	1.102
R(53-75)	1.444	R(118-137)	1.412
R(54-79)	1.501	R(118-147)	1.413
R(55-56)	1.109	R(119-120)	1.109
R(55-57)	1.112	R(119-121)	1.113
R(55-58)	1.112	R(119-122)	1.112
R(59-60)	1.112	R(123-124)	1.098
R(59-61)	1.112	R(123-131)	1.402
R(62-63)	1.099	R(125-126)	1.103
R(64-66)	1.446	R(125-133)	1.404
R(64-73)	1.451	R(127-128)	1.099
R(65-114)	1.414	R(127-129)	1.411
R(65-123)	1.414	R(127-135)	1.402

R(129-141)	1.413	A(1-14-66)	127.6
R(130-149)	1.413	A(15-1-165)	133.6
R(130-153)	1.413	A(1-15-46)	137.0
R(131-132)	1.103	A(1-165-166)	120.0
R(131-133)	1.406	A(1-165-167)	108.1
R(133-134)	1.102	A(8-2-9)	84.7
R(135-136)	1.103	A(8-2-11)	154.8
R(135-139)	1.406	A(8-2-12)	73.5
R(137-138)	1.099	A(8-2-13)	79.0
R(137-143)	1.402	A(8-2-16)	124.0
R(139-140)	1.102	A(8-2-18)	83.8
R(139-145)	1.406	A(2-8-26)	138.7
R(141-142)	1.100	A(9-2-11)	73.9
R(141-145)	1.405	A(9-2-12)	78.4
R(143-144)	1.103	A(9-2-13)	157.8
R(143-151)	1.406	A(9-2-16)	134.2
R(145-146)	1.103	A(9-2-18)	89.1
R(147-148)	1.098	A(2-9-37)	136.6
R(147-155)	1.404	A(11-2-12)	114.0
R(149-150)	1.097	A(11-2-13)	117.2
R(149-157)	1.404	A(11-2-16)	81.1
R(151-152)	1.102	A(11-2-18)	82.6
R(151-155)	1.405	A(2-11-43)	130.7
R(153-154)	1.099	A(12-2-13)	110.8
R(153-161)	1.402	A(12-2-16)	77.6
R(155-156)	1.103	A(12-2-18)	154.9
R(157-158)	1.103	A(2-12-35)	127.5
R(157-159)	1.405	A(13-2-16)	68.0
R(159-160)	1.102	A(13-2-18)	74.2
R(159-161)	1.406	A(2-13-75)	129.1
R(161-162)	1.103	A(16-2-18)	125.3
R(165-166)	0.980	A(2-16-17)	119.1
R(165-167)	1.031	A(2-16-163)	105.5
R(168-169)	0.982	A(2-18-25)	138.2
R(168-170)	1.007	A(4-3-164)	107.0
A(5-1-6)	74.8	A(5-97-23)	124.2
A(5-1-7)	78.4	A(5-97-93)	130.4
A(5-1-10)	122.1	A(6-96-83)	117.6
A(5-1-14)	110.2	A(6-96-93)	121.9
A(5-1-15)	155.3	A(7-38-39)	117.6
A(5-1-165)	71.1	A(7-38-64)	121.8
A(1-5-97)	130.0	A(8-26-27)	118.4
A(6-1-7)	87.6	A(8-26-48)	121.4
A(6-1-10)	84.8	A(9-37-42)	121.9
A(6-1-14)	159.6	A(9-37-76)	118.3
A(6-1-15)	88.9	A(10-45-30)	124.4
A(6-1-165)	120.0	A(10-45-47)	130.0
A(1-6-96)	138.3	A(11-43-36)	124.6
A(7-1-10)	154.9	A(11-43-42)	129.9
A(7-1-14)	74.5	A(12-35-20)	123.4
A(7-1-15)	82.6	A(12-35-48)	131.0
A(7-1-165)	129.7	A(13-75-53)	130.4
A(1-7-38)	138.4	A(13-75-72)	124.2
A(10-1-14)	107.2	A(14-66-24)	124.2
A(10-1-15)	73.3	A(14-66-64)	130.8
A(10-1-165)	74.2	A(15-46-47)	121.9
A(1-10-45)	130.9	A(15-46-59)	118.4
A(14-1-15)	79.3	A(17-16-163)	109.3
A(14-1-165)	79.7	A(18-25-32)	117.9

A(18-25-53)	121.8	A(33-32-59)	110.1
A(20-19-51)	106.5	A(34-32-59)	109.5
A(19-20-35)	112.1	A(32-59-46)	115.4
A(19-20-129)	119.5	A(32-59-60)	110.2
A(19-51-48)	111.2	A(32-59-61)	109.3
A(19-51-55)	118.5	A(35-48-51)	104.5
A(35-20-129)	128.2	A(43-36-111)	129.6
A(20-35-48)	105.5	A(36-43-42)	105.5
A(20-129-127)	119.1	A(36-111-102)	121.8
A(20-129-141)	121.0	A(36-111-109)	118.6
A(24-21-73)	106.6	A(42-37-76)	119.7
A(21-24-52)	118.4	A(37-42-43)	122.6
A(21-24-66)	112.5	A(37-42-44)	132.8
A(21-73-64)	111.2	A(37-76-77)	107.6
A(21-73-68)	118.3	A(37-76-78)	108.1
A(36-22-44)	107.2	A(37-76-83)	115.6
A(22-36-43)	111.6	A(39-38-64)	120.5
A(22-36-111)	118.7	A(38-39-40)	107.9
A(22-44-42)	111.1	A(38-39-41)	108.3
A(22-44-89)	118.5	A(38-64-66)	123.7
A(88-23-97)	111.9	A(38-64-73)	131.6
A(88-23-130)	118.8	A(40-39-41)	106.2
A(23-88-108)	107.1	A(43-42-44)	104.6
A(97-23-130)	129.2	A(42-44-89)	130.3
A(23-97-93)	105.3	A(44-89-90)	108.7
A(23-130-149)	121.6	A(44-89-91)	112.2
A(23-130-153)	118.7	A(44-89-92)	112.0
A(52-24-66)	129.0	A(45-47-46)	122.4
A(24-52-62)	120.9	A(45-47-54)	104.5
A(24-52-94)	119.0	A(47-46-59)	119.6
A(24-66-64)	105.0	A(46-47-54)	133.0
A(32-25-53)	120.3	A(46-59-60)	107.9
A(25-32-33)	107.7	A(46-59-61)	107.8
A(25-32-34)	108.1	A(47-54-79)	130.4
A(25-32-59)	115.0	A(48-51-55)	130.2
A(25-53-74)	132.6	A(50-49-62)	119.2
A(25-53-75)	122.8	A(50-49-86)	120.3
A(27-26-48)	120.2	A(62-49-86)	120.5
A(26-27-28)	108.2	A(49-62-52)	119.7
A(26-27-29)	107.3	A(49-62-63)	120.3
A(26-27-39)	115.3	A(49-86-87)	120.2
A(26-48-35)	122.8	A(49-86-106)	119.6
A(26-48-51)	132.7	A(51-55-56)	108.8
A(28-27-29)	105.9	A(51-55-57)	112.1
A(28-27-39)	110.4	A(51-55-58)	112.0
A(29-27-39)	109.2	A(62-52-94)	120.0
A(27-39-38)	114.8	A(52-62-63)	120.0
A(27-39-40)	110.0	A(52-94-95)	118.9
A(27-39-41)	109.3	A(52-94-106)	119.7
A(31-30-45)	111.6	A(74-53-75)	104.6
A(31-30-65)	118.9	A(53-74-67)	111.2
A(30-31-54)	107.1	A(53-74-119)	130.3
A(45-30-65)	129.5	A(53-75-72)	105.3
A(30-45-47)	105.6	A(54-79-80)	108.7
A(30-65-114)	121.7	A(54-79-81)	112.3
A(30-65-123)	118.6	A(54-79-82)	111.9
A(31-54-47)	111.1	A(56-55-57)	108.4
A(31-54-79)	118.5	A(56-55-58)	107.8
A(33-32-34)	106.2	A(57-55-58)	107.7

A(60-59-61)	105.9	A(104-102-111)	119.5
A(66-64-73)	104.7	A(102-104-105)	118.8
A(64-73-68)	130.5	A(102-104-116)	121.1
A(114-65-123)	119.7	A(102-111-109)	119.6
A(65-114-115)	119.8	A(105-104-116)	120.1
A(65-114-125)	119.5	A(104-116-112)	119.1
A(65-123-124)	118.7	A(104-116-117)	120.5
A(65-123-131)	119.9	A(110-109-111)	118.7
A(72-67-74)	106.9	A(110-109-112)	121.4
A(67-72-75)	112.0	A(111-109-112)	120.0
A(67-72-118)	119.0	A(109-112-113)	119.1
A(67-74-119)	118.4	A(109-112-116)	120.7
A(69-68-70)	107.9	A(113-112-116)	120.1
A(69-68-71)	108.2	A(112-116-117)	120.5
A(69-68-73)	108.5	A(115-114-125)	120.7
A(70-68-71)	107.6	A(114-125-126)	118.8
A(70-68-73)	112.1	A(114-125-133)	121.1
A(71-68-73)	112.4	A(137-118-147)	119.8
A(75-72-118)	129.0	A(118-137-138)	118.7
A(72-118-137)	118.8	A(118-137-143)	119.9
A(72-118-147)	121.4	A(118-147-148)	119.7
A(74-119-120)	108.7	A(118-147-155)	119.6
A(74-119-121)	112.0	A(120-119-121)	108.1
A(74-119-122)	112.0	A(120-119-122)	108.3
A(77-76-78)	106.0	A(121-119-122)	107.5
A(77-76-83)	109.1	A(124-123-131)	121.4
A(78-76-83)	110.1	A(123-131-132)	119.1
A(76-83-84)	110.3	A(123-131-133)	120.8
A(76-83-85)	109.2	A(126-125-133)	120.1
A(76-83-96)	115.0	A(125-133-131)	119.1
A(80-79-81)	108.2	A(125-133-134)	120.5
A(80-79-82)	108.0	A(128-127-129)	118.7
A(81-79-82)	107.6	A(128-127-135)	121.5
A(84-83-85)	106.0	A(129-127-135)	119.8
A(84-83-96)	108.0	A(127-129-141)	120.0
A(85-83-96)	107.9	A(127-135-136)	119.3
A(83-96-93)	120.5	A(127-135-139)	120.6
A(87-86-106)	120.2	A(129-141-142)	119.9
A(86-106-94)	120.5	A(129-141-145)	119.6
A(86-106-107)	120.1	A(149-130-153)	119.6
A(88-108-93)	111.2	A(130-149-150)	119.7
A(88-108-98)	118.4	A(130-149-157)	119.6
A(90-89-91)	108.2	A(130-153-154)	118.6
A(90-89-92)	108.0	A(130-153-161)	119.9
A(91-89-92)	107.6	A(132-131-133)	120.1
A(96-93-97)	122.9	A(131-133-134)	120.5
A(96-93-108)	132.4	A(136-135-139)	120.1
A(97-93-108)	104.5	A(135-139-140)	120.3
A(93-108-98)	130.4	A(135-139-145)	119.4
A(95-94-106)	121.3	A(138-137-143)	121.5
A(94-106-107)	119.4	A(137-143-144)	119.2
A(99-98-100)	108.3	A(137-143-151)	120.7
A(99-98-101)	107.9	A(140-139-145)	120.3
A(99-98-108)	108.6	A(139-145-141)	120.7
A(100-98-101)	107.8	A(139-145-146)	120.1
A(100-98-108)	112.2	A(142-141-145)	120.5
A(101-98-108)	111.9	A(141-145-146)	119.2
A(103-102-104)	120.8	A(144-143-151)	120.1
A(103-102-111)	119.7	A(143-151-152)	120.4

A(143-151-155)	119.3
A(148-147-155)	120.6
A(147-155-151)	120.8
A(147-155-156)	119.1
A(150-149-157)	120.7
A(149-157-158)	119.0
A(149-157-159)	120.9
A(152-151-155)	120.4
A(151-155-156)	120.1
A(154-153-161)	121.5
A(153-161-159)	120.7
A(153-161-162)	119.2
A(158-157-159)	120.0
A(157-159-160)	120.4
A(157-159-161)	119.1
A(160-159-161)	120.5
A(159-161-162)	120.1
A(166-165-167)	111.6
A(169-168-170)	105.5

Table S9. Absolute energies of gadolinium complexes under consideration (RI-DFT/PBE0).

Compound	Energy, a.u.
$[Gd_2(Q_2Q_3)_3(H_2O)_2]$	-4561.89239663696
$[Gd_2(Q_2Q_3)_3(H_2O)_4]$	-4714.64434068488

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