PARASHIFT Probes: Solution NMR and X-ray Structural Studies of Macrocyclic Ytterbium and Yttrium Complexes

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NMR and DFT data for [Y.L[1]]

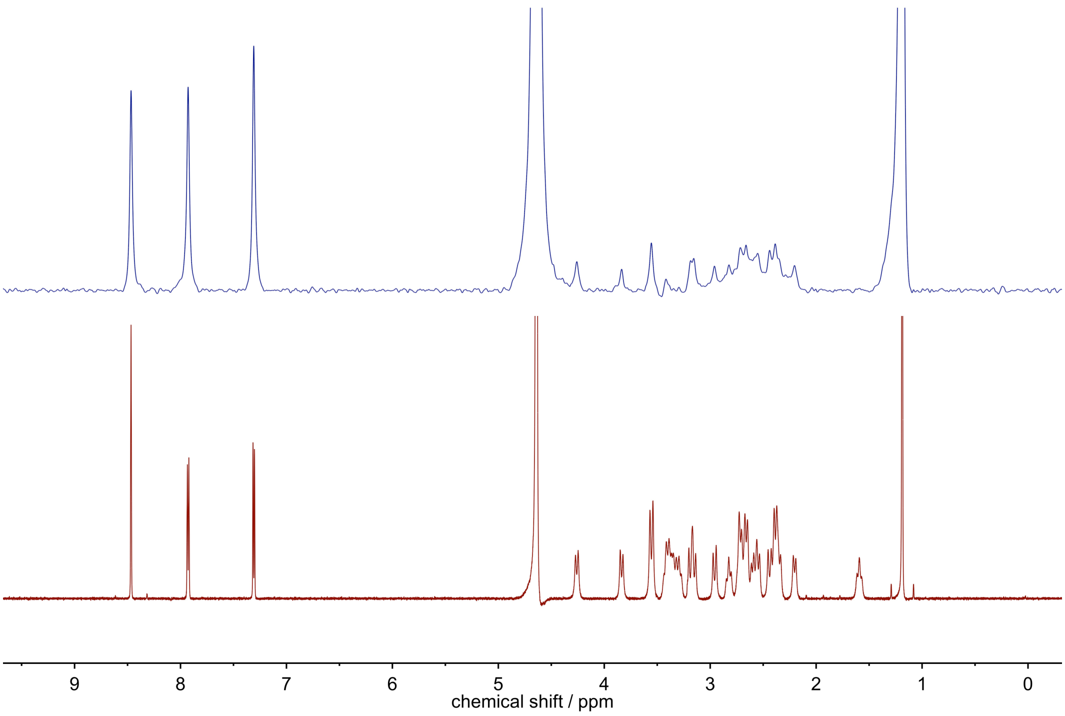

Figure S1. ^{1}H, (*lower*) and ^{1}H with ^{1}H decoupling NMR spectra (*upper*) for **[Y.L^1]** (600 MHz, 298 K, D_2O, pD 6).

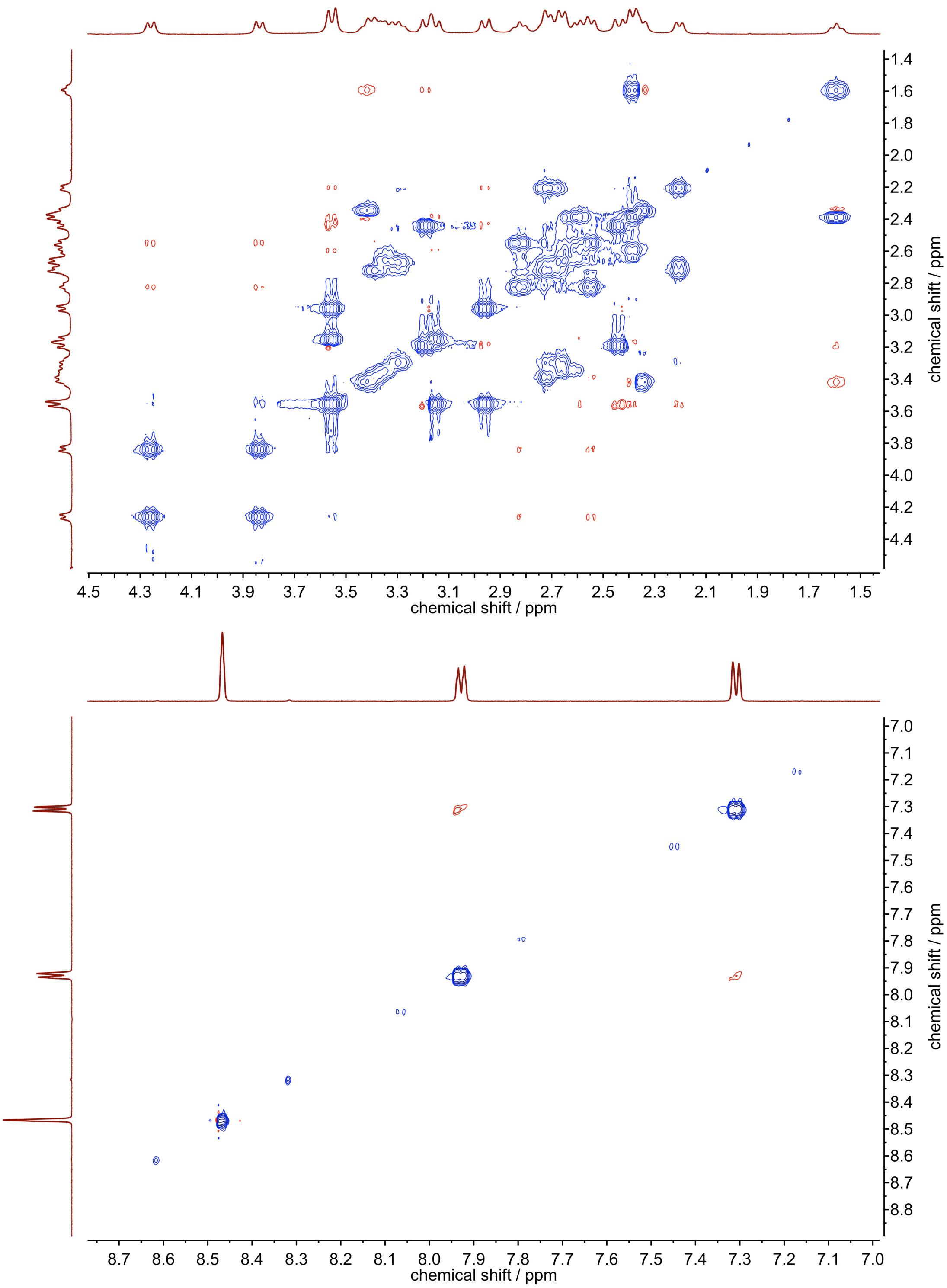

Figure S2. ^1H-^1H 2D NOESY/EXSY NMR spectrum (mixing time 500 ms) of **[Y.L[1]]** (600 MHz, D_2O, 298 K). (*upper*) aliphatic region; (*lower*) aromatic region.

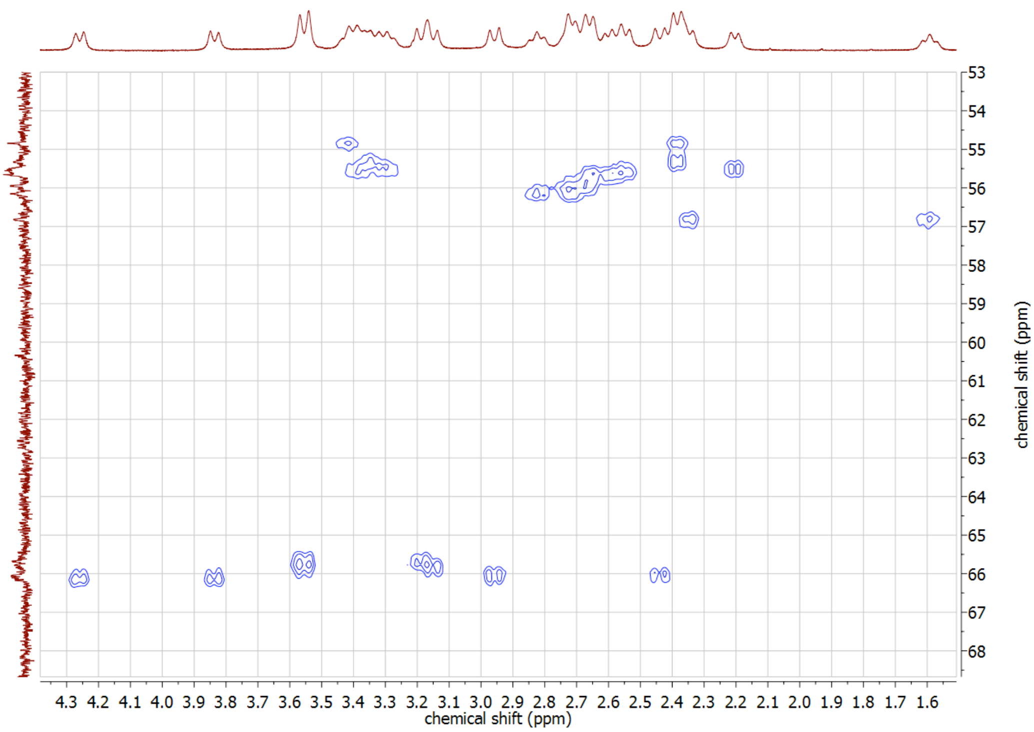

Figure S3. Aliphatic part of the ^{1}H-^{13}C HSQC NMR spectrum (14.1 T, D_2O, 298 K) for **[Y.L[1]]**.

Table S1. Optimized geometry (M06-2X/cc-pVDZ SMD(water)) of **[Y.L[1]]** conformers with and without explicit water molecules.

	Λ-λλλλ			Λ-λλλλ+H_2O			Λ-δδδδ			Λ-δδδδ+H_2O		
Y	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
C	0.5699	-3.0789	-0.6257	0.5635	-3.0929	-0.6099	1.3956	-2.8875	-0.4093	1.4122	-2.9209	-0.3183
C	-0.4082	3.1796	-0.5534	-0.3725	3.2087	-0.5183	-1.2955	2.9408	-0.4543	-1.2663	3.0183	-0.2878
C	-3.1277	-0.4071	-0.6608	-3.1164	-0.4190	-0.6293	-2.9033	-1.3549	-0.4558	-2.9286	-1.3461	-0.3718
O	0.8321	-4.1074	-1.2587	0.7992	-4.1158	-1.2619	2.1265	-3.7848	-0.8471	2.1579	-3.8212	-0.7278
O	0.9347	-1.8927	-0.9698	0.9462	-1.9081	-0.9408	1.3788	-1.6796	-0.8468	1.4068	-1.7178	-0.7612
O	-4.1595	-0.5707	-1.3220	-4.1438	-0.5855	-1.2966	-3.8209	-2.0350	-0.9327	-3.8603	-2.0297	-0.8178
O	-0.5419	4.2294	-1.1969	-0.4834	4.2547	-1.1688	-1.9407	3.8569	-0.9802	-1.8495	3.9742	-0.8199
O	-0.8100	2.0227	-0.9406	-0.7617	2.0501	-0.9212	-1.2678	1.7287	-0.8801	-1.3083	1.8102	-0.7143
O	-1.9530	-0.7897	-1.0202	-1.9445	-0.8230	-0.9694	-1.6788	-1.4036	-0.8397	-1.7133	-1.4128	-0.7770
N	2.0998	0.0000	1.6510	2.0884	0.0000	1.6757	2.1184	0.0000	1.5238	2.1079	0.0000	1.6253
N	-0.0136	-2.0852	1.5717	-0.0011	-2.0979	1.5889	-0.0108	-2.1009	1.5291	-0.0228	-2.1113	1.5763
N	-2.1013	0.0053	1.5615	-2.0906	0.0059	1.5814	-2.1127	-0.0161	1.5193	-2.1017	-0.0088	1.5851
N	0.0151	2.0799	1.6374	0.0034	2.0920	1.6722	0.0051	2.1170	1.5453	0.0166	2.1201	1.6892
N	2.2034	0.9302	-0.9506	2.2058	1.0197	-0.8764	1.9317	1.5262	-0.8544	1.9152	1.6214	-0.6814
C	1.9185	-1.0125	2.7091	1.9242	-1.0183	2.7304	2.2783	-1.3311	2.1566	2.2653	-1.3439	2.2271
C	1.3148	-2.2980	2.1816	1.3251	-2.3057	2.2021	0.9572	-1.9042	2.6289	0.9401	-1.9222	2.6816
C	-1.0536	-1.9997	2.6135	-1.0404	-1.9998	2.6303	-1.3573	-2.3299	2.0954	-1.3696	-2.3361	2.1406
C	-2.3258	-1.3549	2.0958	-2.3128	-1.3561	2.1125	-1.9943	-1.0401	2.5811	-1.9979	-1.0465	2.6342
C	-1.9822	0.9853	2.6554	-1.9849	0.9802	2.6816	-2.2898	1.3155	2.1360	-2.2819	1.3091	2.2289
C	-1.3439	2.2792	2.1869	-1.3544	2.2805	2.2233	-0.9711	1.8754	2.6340	-0.9702	1.8546	2.7575
C	0.9942	1.9522	2.7327	0.9807	1.9433	2.7668	1.3435	2.3314	2.1397	1.3471	2.3138	2.3001
C	2.2974	1.3303	2.2655	2.2852	1.3288	2.2939	1.9980	1.0304	2.5857	1.9897	0.9990	2.7133
C	-0.2785	-3.1927	0.6441	-0.2673	-3.2128	0.6708	0.3907	-3.2390	0.6883	0.3731	-3.2590	0.7485
C	-3.2171	0.3435	0.6688	-3.2069	0.3449	0.6904	-3.2419	-0.3331	0.6311	-3.2383	-0.3001	0.6991
C	0.3352	3.2329	0.7830	0.3263	3.2574	0.8399	-0.4147	3.2813	0.7494	-0.3857	3.3092	0.9268
C	3.2761	-0.3325	0.8295	3.2594	-0.3341	0.8454	3.3054	0.2523	0.6824	3.2949	0.2753	0.7938
C	3.3640	0.5638	-0.3790	3.3604	0.5756	-0.3512	3.1216	1.4208	-0.2463	3.1205	1.4577	-0.1219
C	4.5831	1.0042	-0.8812	4.5882	0.9612	-0.8796	4.1406	2.3447	-0.4749	4.1780	2.3215	-0.4120
C	4.6005	1.8511	-1.9879	4.6240	1.8402	-1.9602	3.8999	3.4179	-1.3220	3.9689	3.3747	-1.2919
C	3.4020	2.2607	-2.5765	3.4334	2.3506	-2.4832	2.6528	3.5597	-1.9461	2.7086	3.5679	-1.8758
C	2.2289	1.7546	-2.0056	2.2540	1.8917	-1.8914	1.7154	2.5610	-1.6850	1.7246	2.6437	-1.5323
C	3.3139	3.2269	-3.7552	3.3525	3.3841	-3.6040	2.3410	4.7756	-2.8136	2.4412	4.7359	-2.8203
C	2.5810	4.4970	-3.2955	2.7929	4.6904	-3.0174	0.9190	4.7233	-3.3757	0.9859	4.7601	-3.2934
C	4.7027	3.6131	-4.2652	4.7285	3.6566	-4.2124	2.4820	6.0361	-1.9457	2.7424	6.0483	-2.0823
C	2.5322	2.5676	-4.9013	2.4127	2.8785	-4.7096	3.3385	4.8409	-3.9784	3.3619	4.6114	-4.0428
H	1.2651	-0.5851	3.4807	1.2772	-0.5983	3.5113	2.9701	-1.2659	3.0148	2.9510	-1.2977	3.0921
H	2.8862	-1.2356	3.1943	2.8986	-1.2383	3.2038	2.7473	-2.0068	1.4291	2.7399	-2.0052	1.4908
H	1.9732	-2.7377	1.4199	1.9865	-2.7464	1.4432	1.1470	-2.8669	3.1373	1.1248	-2.8882	3.1861
H	1.2431	-3.0342	3.0020	1.2532	-3.0411	3.0237	0.5060	-1.2314	3.3697	0.4848	-1.2541	3.4240

H	-0.6486	-1.4164	3.4511	-0.6338	-1.4098	3.4623	-1.3062	-3.0417	2.9388	-1.3228	-3.0523	2.9810
H	-1.2896	-3.0054	3.0057	-1.2798	-3.0012	3.0320	-1.9818	-2.7969	1.3234	-1.9966	-2.7970	1.3674
H	-2.7500	-1.9679	1.2880	-2.7381	-1.9687	1.3052	-2.9940	-1.2670	2.9927	-3.0015	-1.2689	3.0395
H	-3.0788	-1.3269	2.9040	-3.0646	-1.3290	2.9219	-1.4040	-0.6165	3.4025	-1.4082	-0.6384	3.4636
H	-1.3778	0.5360	3.4546	-1.3838	0.5300	3.4827	-2.9998	1.2614	2.9802	-3.0040	1.2361	3.0619
H	-2.9758	1.2055	3.0864	-2.9825	1.1909	3.1080	-2.7336	1.9887	1.3898	-2.7154	2.0005	1.4940
H	-1.9617	2.7370	1.4016	-1.9740	2.7427	1.4418	-1.1600	2.8193	3.1757	-1.1680	2.7855	3.3196
H	-1.3113	2.9981	3.0253	-1.3246	2.9927	3.0678	-0.5204	1.1760	3.3501	-0.5309	1.1396	3.4653
H	0.5439	1.3377	3.5233	0.5297	1.3143	3.5454	1.2720	2.9974	3.0186	1.2717	2.9552	3.1977
H	1.2061	2.9413	3.1780	1.1910	2.9240	3.2311	1.9685	2.8497	1.4035	1.9839	2.8489	1.5863
H	2.7773	1.9852	1.5253	2.7618	1.9883	1.5562	2.9986	1.2636	2.9922	2.9901	1.2122	3.1319
H	2.9931	1.2542	3.1204	2.9830	1.2504	3.1471	1.4196	0.5933	3.4092	1.4031	0.5445	3.5211
H	-1.3311	-3.1645	0.3238	-1.3242	-3.1967	0.3645	-0.4987	-3.6066	0.1547	-0.5105	-3.6081	0.1930
H	-0.0967	-4.1717	1.1200	-0.0680	-4.1879	1.1477	0.7880	-4.0706	1.2944	0.7382	-4.0983	1.3647
H	1.4095	3.2309	0.5397	1.4067	3.2764	0.6257	0.4764	3.7735	0.3298	0.5109	3.8063	0.5262
H	0.1127	4.1873	1.2908	0.0751	4.2042	1.3487	-0.9303	4.0329	1.3703	-0.8972	4.0494	1.5659
H	3.1887	-1.3753	0.4906	3.1614	-1.3716	0.4948	3.4714	-0.6433	0.0664	3.4679	-0.6078	0.1610
H	4.2052	-0.2498	1.4212	4.1910	-0.2684	1.4357	4.2004	0.4052	1.3093	4.1899	0.4181	1.4242
H	5.5105	0.6983	-0.3970	5.5096	0.5849	-0.4351	5.0988	2.2306	0.0317	5.1488	2.1661	0.0584
H	5.5589	2.1989	-2.3730	5.5885	2.1397	-2.3700	4.6844	4.1600	-1.4831	4.7911	4.0567	-1.5179
H	3.1409	4.9984	-2.4908	3.4649	5.0875	-2.2410	0.1640	4.6997	-2.5745	0.2830	4.8413	-2.4496
H	1.5716	4.2704	-2.9201	1.8005	4.5353	-2.5664	0.7687	3.8422	-4.0180	0.7314	3.8565	-3.8682
H	2.4840	5.1998	-4.1374	2.6957	5.4475	-3.8109	0.7380	5.6210	-3.9846	0.8328	5.6304	-3.9480
H	4.5984	4.3039	-5.1145	4.6289	4.3946	-5.0216	2.2606	6.9312	-2.5470	2.5680	6.9031	-2.7534
H	5.2654	2.7323	-4.6102	5.1687	2.7417	-4.6376	3.5017	6.1384	-1.5454	3.7880	6.0912	-1.7430
H	5.2946	4.1200	-3.4886	5.4286	4.0650	-3.4686	1.7790	6.0059	-1.0984	2.0888	6.1604	-1.2032
H	2.4763	3.2576	-5.7570	2.3862	3.6071	-5.5341	3.1307	5.7263	-4.5985	3.1874	5.4528	-4.7307
H	1.5036	2.3171	-4.6022	1.3814	2.7533	-4.3461	3.2570	3.9463	-4.6144	3.1666	3.6742	-4.5862
H	3.0298	1.6439	-5.2343	2.7605	1.9148	-5.1124	4.3752	4.9156	-3.6177	4.4225	4.6257	-3.7504
H	1.2500	2.0231	-2.4109	1.2902	2.2595	-2.2455	0.7275	2.5829	-2.1454	0.7204	2.7165	-1.9511
H	-3.1815	1.4155	0.4236	-3.1706	1.4153	0.4384	-3.5295	0.5824	0.0919	-3.4928	0.6180	0.1479
H	-4.1921	0.1384	1.1437	-4.1816	0.1437	1.1678	-4.1203	-0.6795	1.2009	-4.1286	-0.6116	1.2711
O				-0.2845	0.3989	-3.1984				0.0709	0.1257	-2.5542
H				0.4805	0.7366	-3.6879				-0.4676	0.9182	-2.7208
H				-0.5138	1.1301	-2.5924				0.9476	0.3620	-2.8978

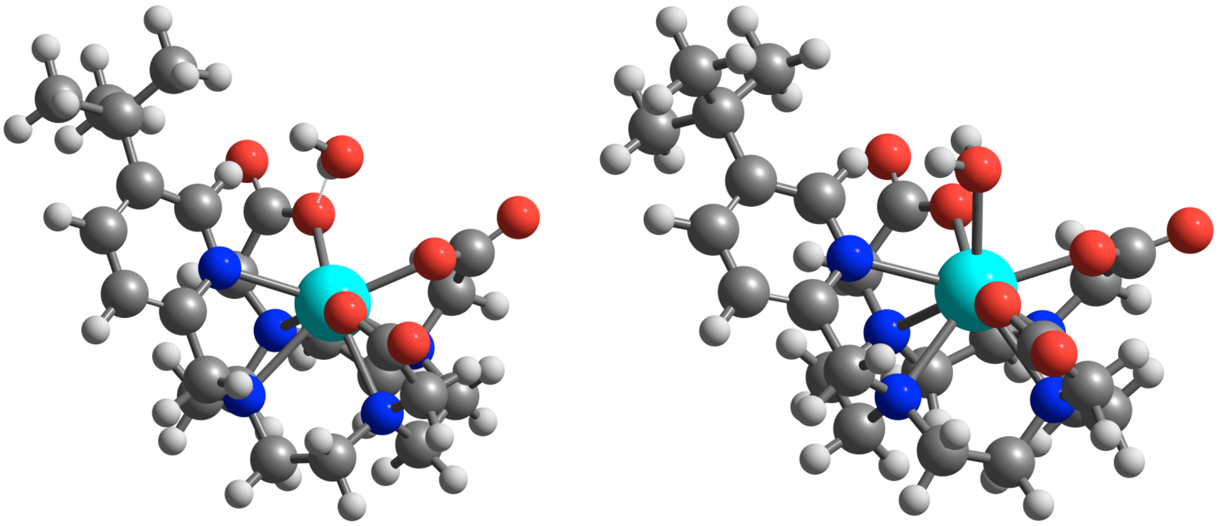

Figure S4. Optimized structure of *Λ-λλλλ* (left) and *Λ-δδδδ* (right) with explicit water molecule showing different types of interactions with water (hydrogen bonding *vs.* direct coordination).

NMR and DFT data for [Y.L^2]

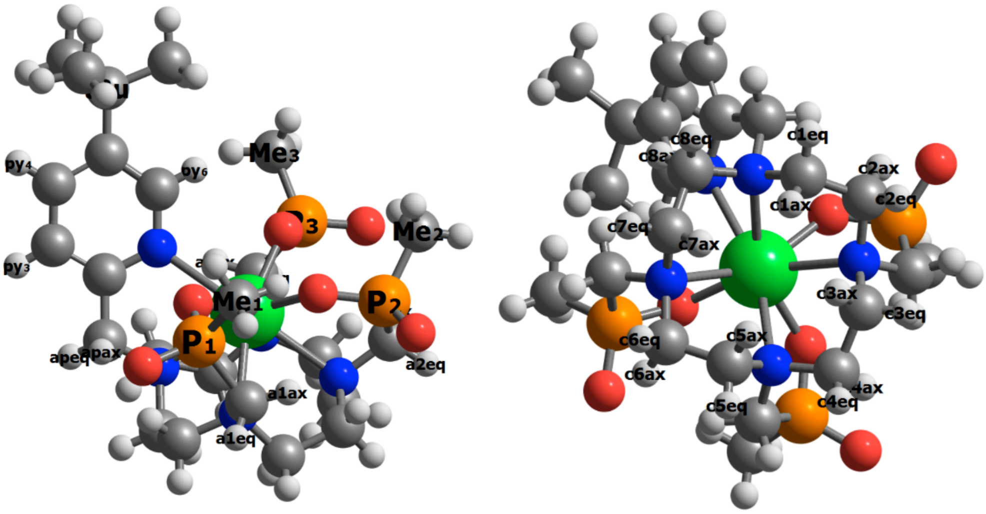

Figure S5. Labels for atoms used in the assignment tables. The cyclen protons and carbons are labeled with 'c' and ordered clockwise, where 'ax' stands for axial and 'eq' stands for equatorial protons. Exocyclic methylene protons are labeled with 'a' and numbered the same way, and the pyridine arm is labeled 'ap'.

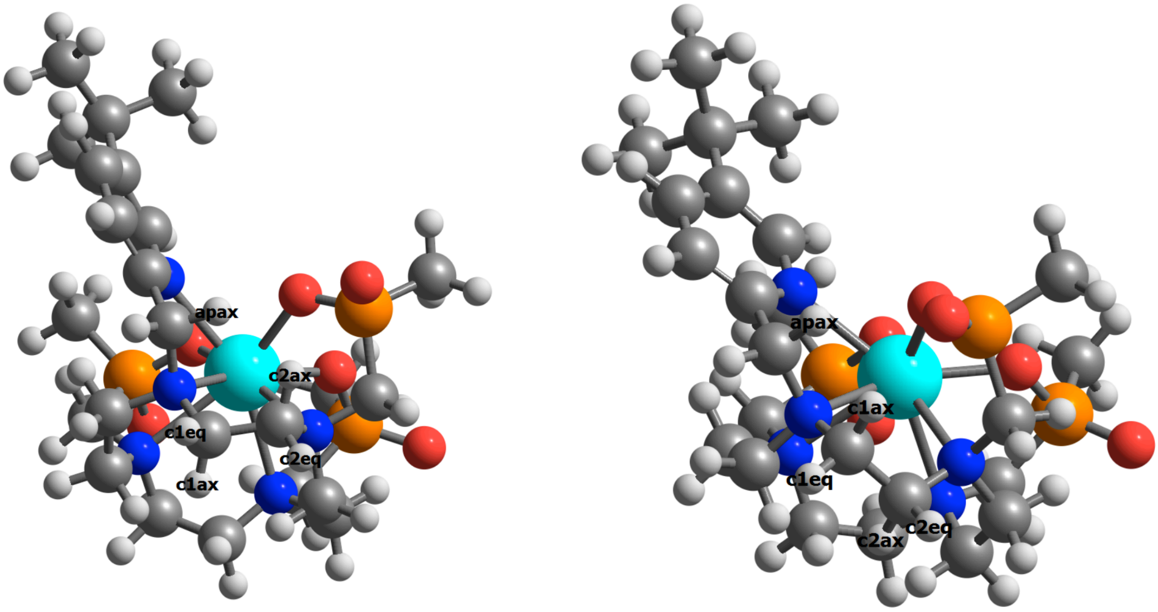

Figure S6. Difference in distances between 'apax' proton and nearest cyclen protons of (RRR)-Λ-(λλλλ) (left) and (RRR)-Λ-(δδδδ) (right) of **[Y.L^2]** used to discriminate structures based on NOESY cross-peaks. Distances for (RRR)-Λ-(λλλλ) in Å: apax-c2ax 2.023; apax-a1eq 2.704; apax-c2eq 3.545; apax-c1ax 3.620, and for (RRR)-Λ-(δδδδ): apax-c1ax 2.025; apax-c1eq 3.030; apax-c2eq 4.424; apax-a2ax 4.438 Å.

Table S2. Assignment of ^{31}P, ^{13}C and ^{1}H resonances of major conformer of **[Y.L^2]**

Label	Shift, ppm
P1	43.9
P2	43.3
P3	41
c1	50.1
c2	53.2
c3	51.6
c4	53.9
c5	51.8
c6	53.5

c7	51.6
c8	52.6
a1	56.7/56.0
a2	55.9/55.3
a3	56.3/55.7
ap	59.4
py3	123.6
py4	138.4
py6	145.2
m1	15.6
m2	15.7
m3	16.3
tBu	33.3
c1ax	3.51
c1eq	2.47
c2ax	3.58
c2eq	2.59
c3ax	3.41
c3eq	2.40
c4ax	3.53
c4eq	2.50
c5ax	3.42
c5eq	2.32
c6ax	3.82
c6eq	2.48
c7ax	3.37
c7eq	2.29
c8ax	2.98
c8eq	2.43
a1ax	3.43
a1eq	2.59
a2ax	3.61
a2eq	2.59
a3ax	2.77
a3eq	2.48
apax	4.55
apeq	3.65
py3	7.35
py4	7.97
py6	8.60
Me1	1.26
Me2	1.44
Me3	1.26
tBu	1.24

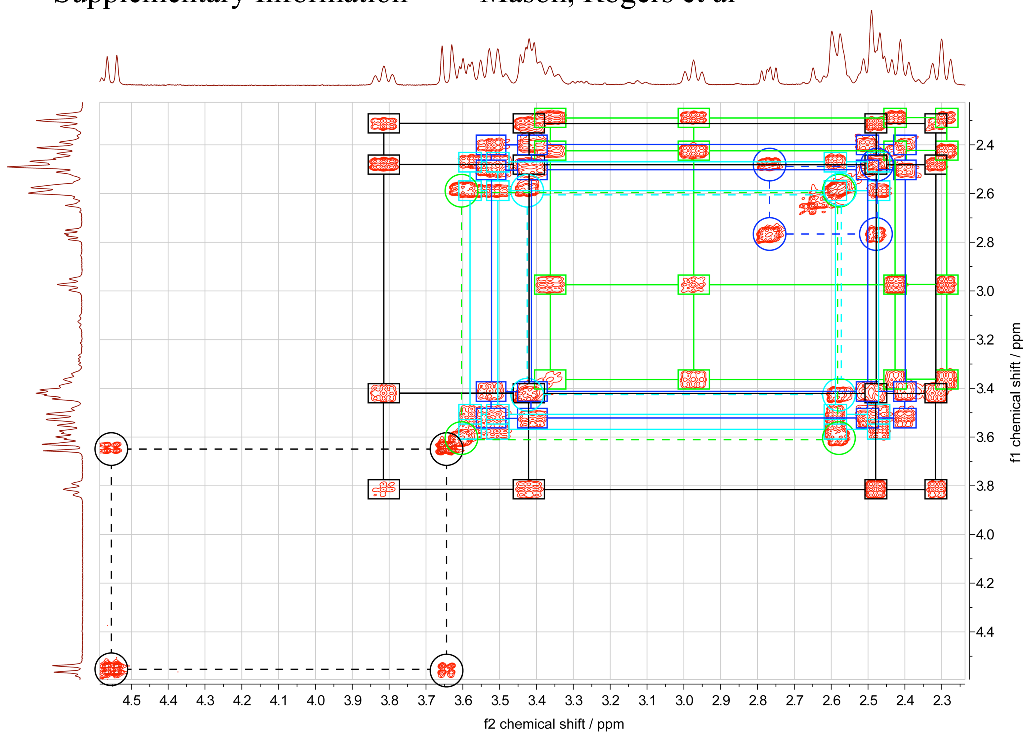

Figure S7. Aliphatic part of the ^{1}H-^{1}H TOCSY NMR spectrum (14.1 T, D_2O, pD 6, 298 K) for **[Y.L^2]**. Arm pairs are shown with dashed lines and groups of four *J*-coupled cyclen protons are shown with solid lines.

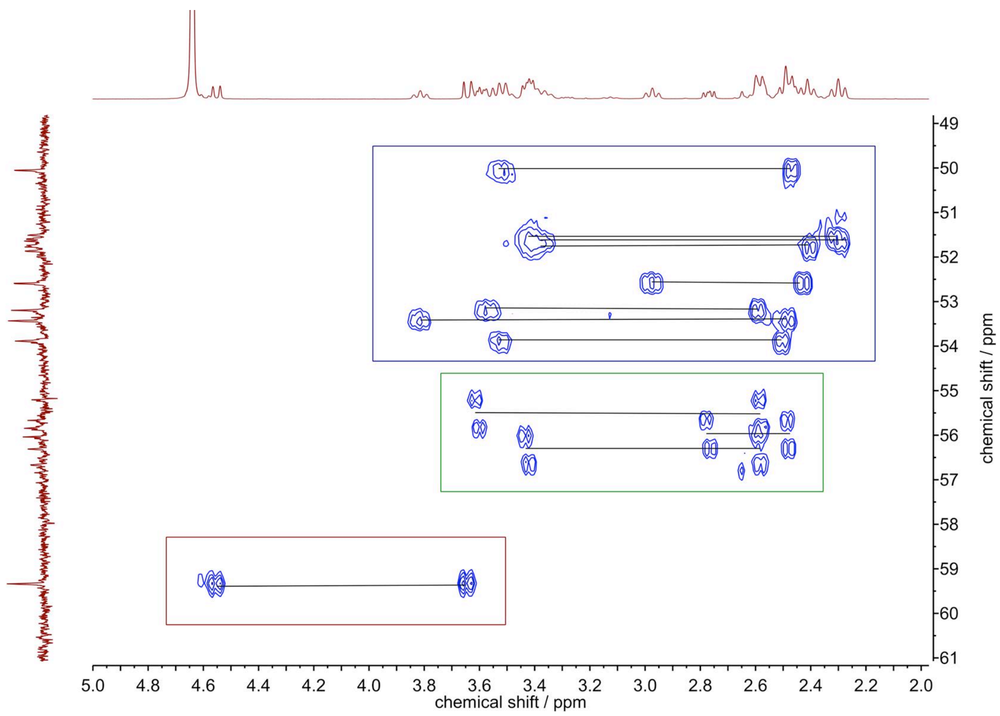

Figure S8. Aliphatic part of the ^{1}H-^{13}C HSQC NMR spectrum (14.1 T, D_2O, pD 6, 298 K) for **[Y.L^2]**, showing cyclen-CH_2 (*blue* box), PCH_2N (*green*) and pyCH_2N resonances (*red* box).

NMR data for [Y.L[3]]

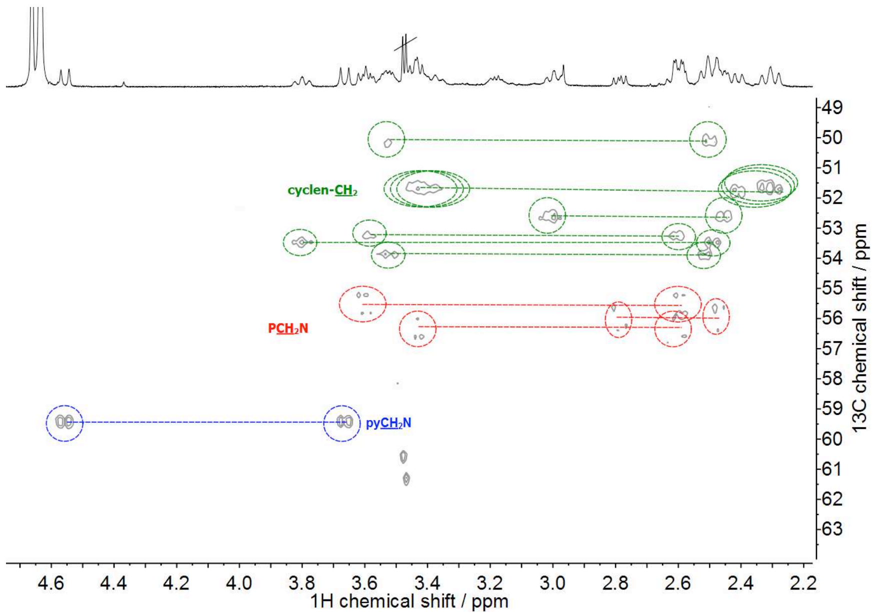

Figure S9. ^{1}H-^{13}C HSQC NMR spectrum (600 MHz, 298 K, pD 7) of the aliphatic region of **[Y.L^{3}]$^{2-}$**. The cyclen-CH$_2$ resonances are highlighted in green, pyCH$_2$N in blue, and PCH$_2$N in red.

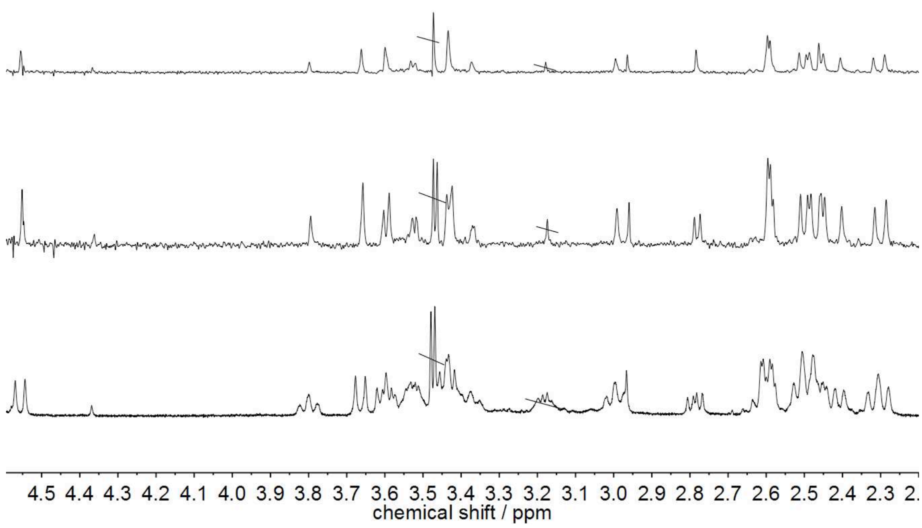

Figure 10. ^{1}H, (*lower*), ^{1}H with ^{1}H decoupling (*centre*), and ^{1}H with 1H and ^{31}P decoupling (*top*) NMR spectra (600 MHz, 298 K, pD 7) of **[Y.L^{3}]$^{2-}$**. Crossed out peaks are from a (hydroxymethyl)(methyl)phosphinic acid impurity.

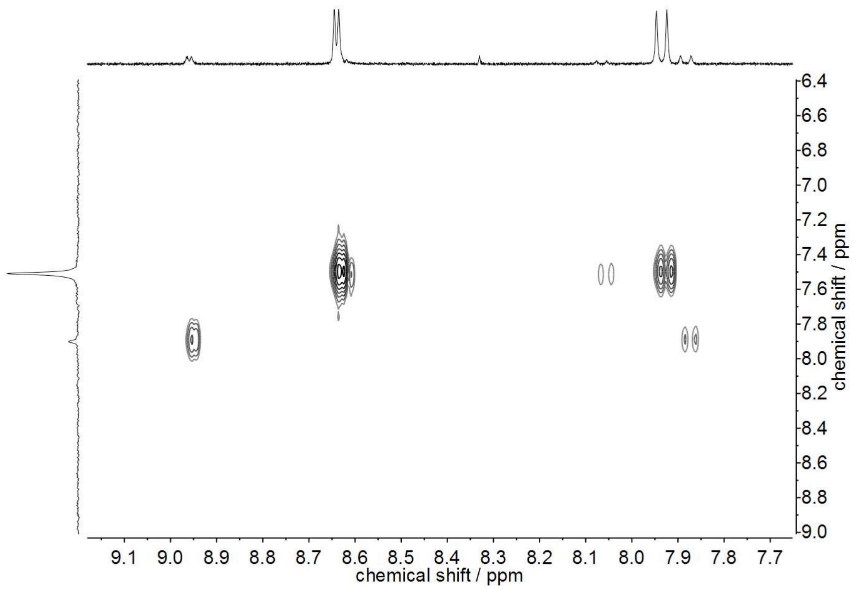

Figure S11. ^{1}H-^{31}P HMBC NMR spectrum (600 MHz, 298 K, D_2O, pD 7), of **$[Y.L^3]^{2-}$** shows correlations between the phosphonate ^{31}P resonance at 7.5 ppm and the aromatic protons of the major isomer (8.64 and 7.93 ppm), as well as cross peaks belonging to the minor conformer (^{31}P = 7.9 ppm, ^{1}H = 8.96, 7.88 ppm).

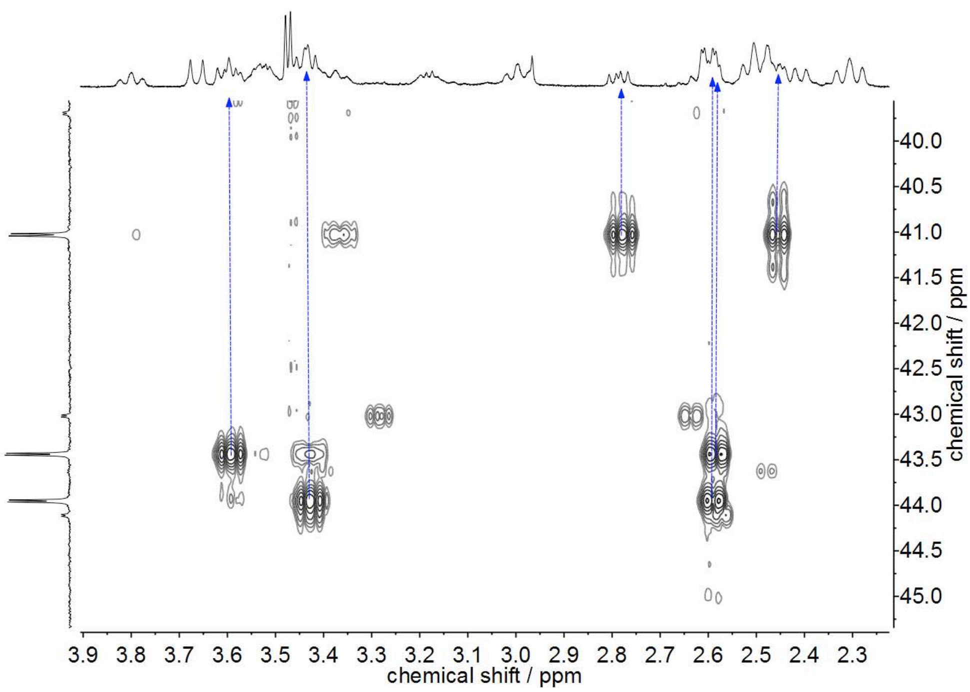

Figure S12. ^{1}H ^{31}P HMBC NMR spectrum, (600 MHz, 298 K, D_2O, pD 7), of **$[Y.L^3]^{2-}$**.

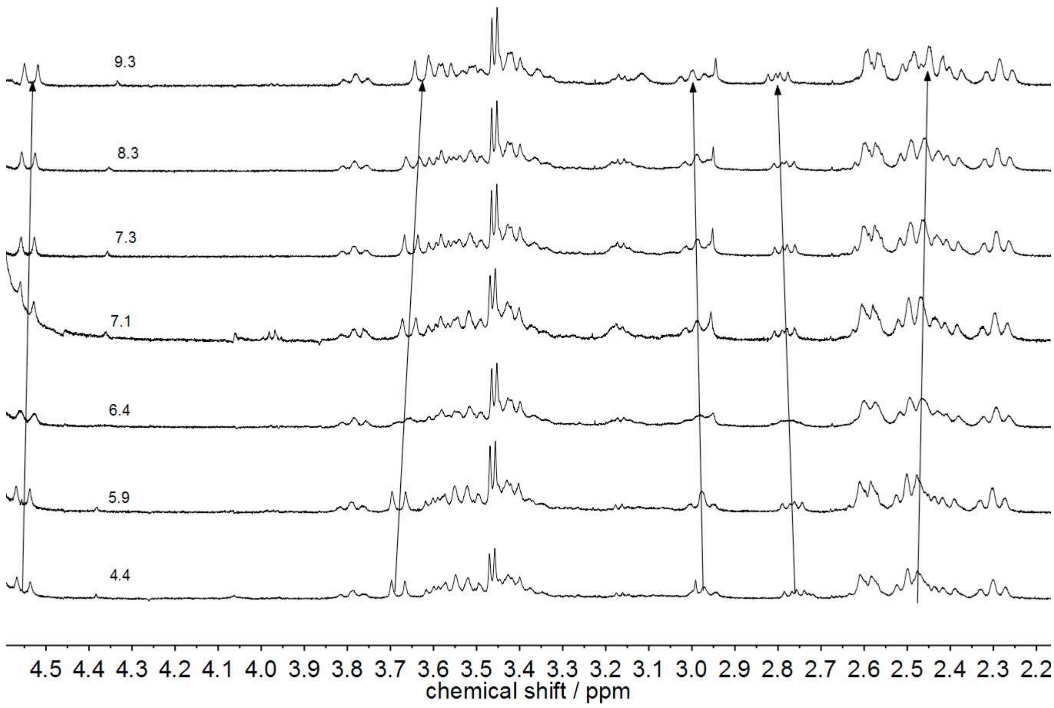

Figure S13. Aliphatic region of the ^{1}H NMR spectrum of $[Y.L^3]^{2-}$ (500 MHz, 295 K, D_2O), varying the pD from 4.4 to 9.3

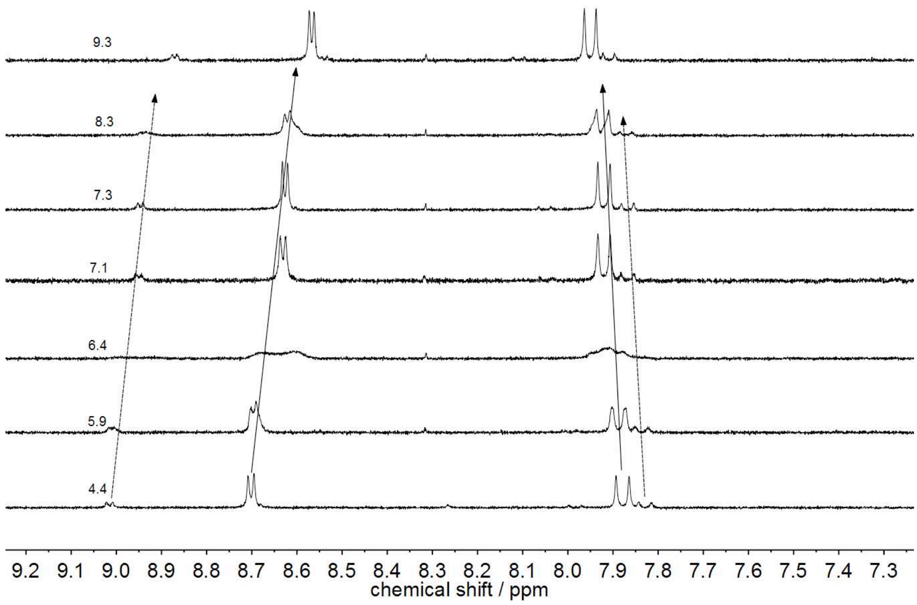

Figure S14. Aromatic region of the ^{1}H NMR spectrum of $[Y.L^3]^{2-}$, (500 MHz, 295 K, D_2O), varying pD from 4.4 to 9.3.

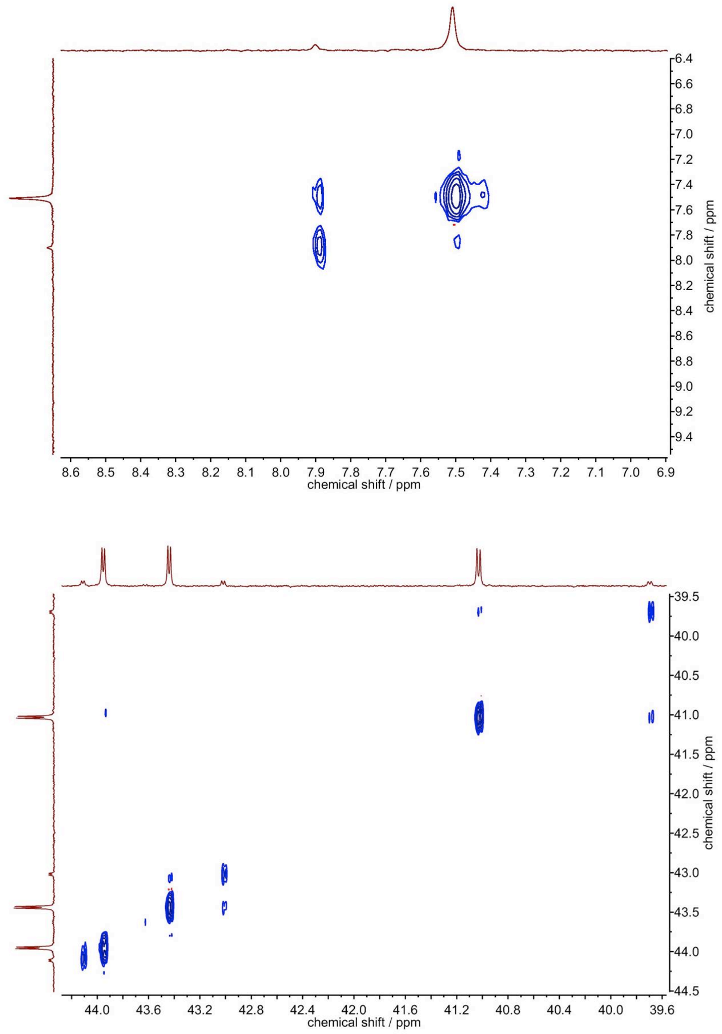

Figure S15. ^{31}P-^{31}P 2D NOESY/EXSY NMR spectrum (14.1 T, D_2O, 295 K, pD 7, mixing time = 300 ms) of the phosphonate ^{31}P (*upper*) and phosphinate ^{31}P resonances (*lower*) for **$[Y.L^3]^{2-}$**, showing exchange correlations (*blue*).

Structure and analysis of [Yb.L^1] magnetic properties

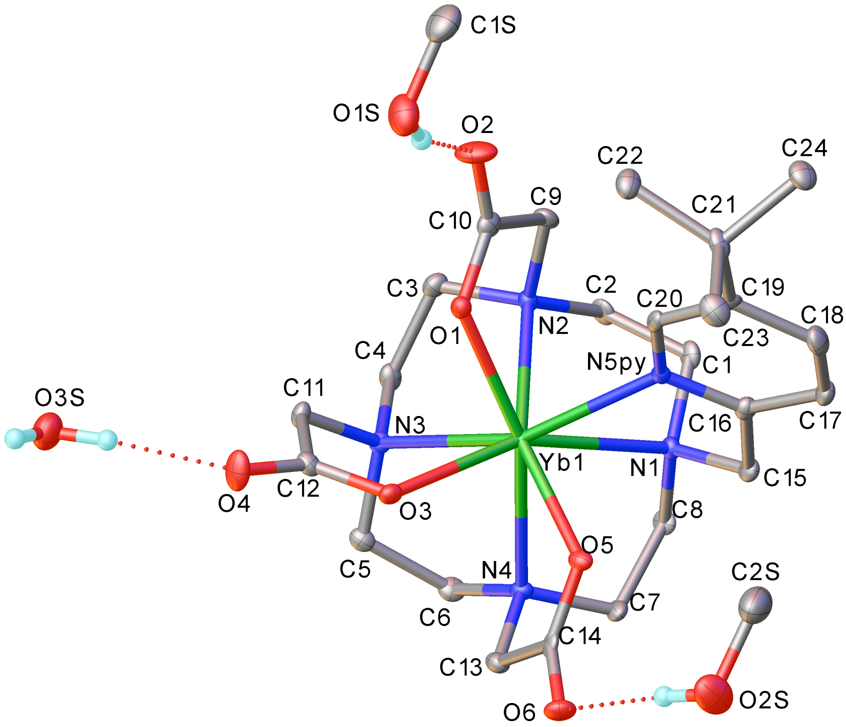

Figure S16. X-ray molecular structure of **[Yb.L^1]**·2MeOH·H_2O. Thermal ellipsoids are drawn at the 50% probability level; H atoms are omitted for clarity, except those of hydroxyl groups and water.

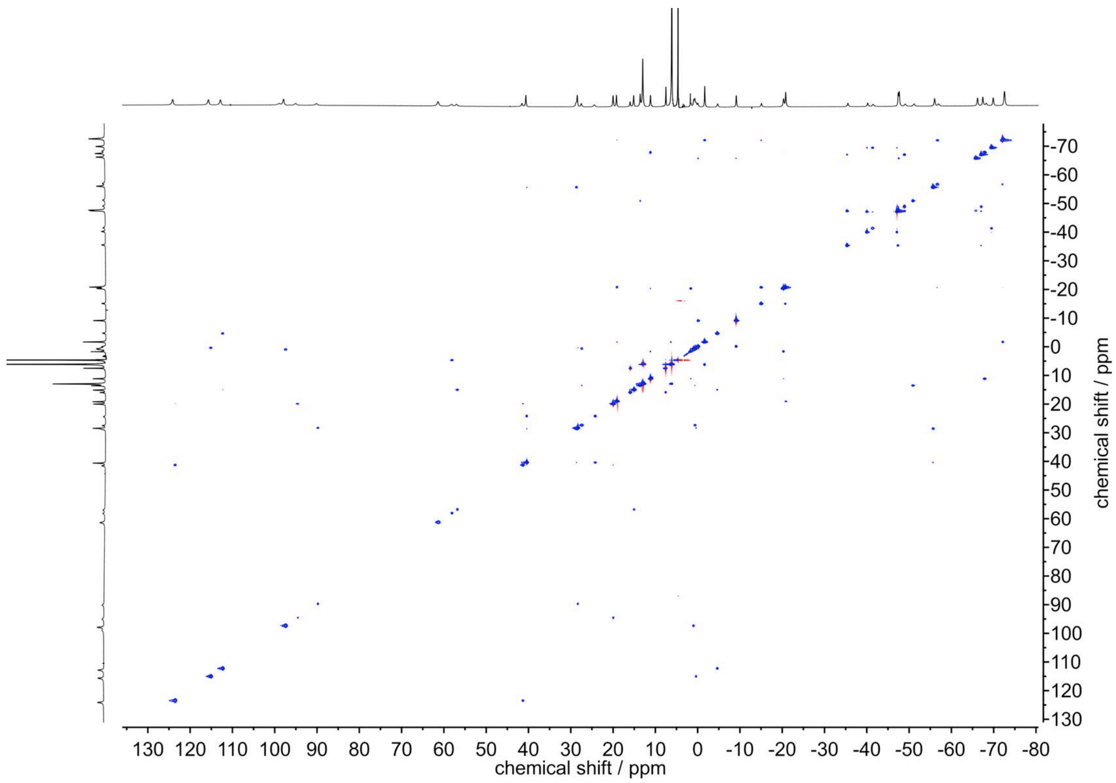

Figure S17. ^1H-^1H 2D EXSY NMR spectrum of **[Yb.L^1]** (4.7 T, D_2O, 295 K), acquired using a 5 ms mixing time.

Table S3. Assigned paramagnetic shifts of major conformer of **[Yb.L[1]]** protons (4.7 T, D_2O, 295 K) and phosphorus atoms.

Label	Shift, ppm	Width, Hz	R_1, s^{-1}	Diamagnetic reference, ppm
c7ax	124.13	89	105	3.5
c1ax	112.84	93	110	3.5
c5ax	115.68	94	115	3.5
c3ax	97.92	82	99	3.5
py6	61.38	105	231	8.47
c7eq	40.62	51	61	2.5
c8eq	28.47	52	69	2.5
c6eq	15.13	51	62	2.5
c3eq	19.2	46	56	2.5
c4eq	20	53	69	2.5
c1eq	11.15	49	61	2.5
c5eq	13.59	52	47	2.5
py4	7.51	35	4.6	7.93
tBu	6.12	33	6.6	1.19
c2eq	4.71	-	-	2.5
c8ax	0.68	90	91	3.5
py3	-1.68	41	16	7.31
apeq	-9.13	49	45	3.84
c4ax	-20.31	69	79	3.5
a2eq	-20.82	55	52	2.5
a3eq	-47.45	54	46	2.5
a1eq	-47.68	52	48	2.5
c6ax	-56.03	68	83	3.5
apax	-66.18	66	78	4.26
a3ax	-67.43	62	69	3.5
a1ax	-69.89	66	78	3.5
a2ax	-72.55	71	78	3.5
c2ax	-72.55	71	78	3.5

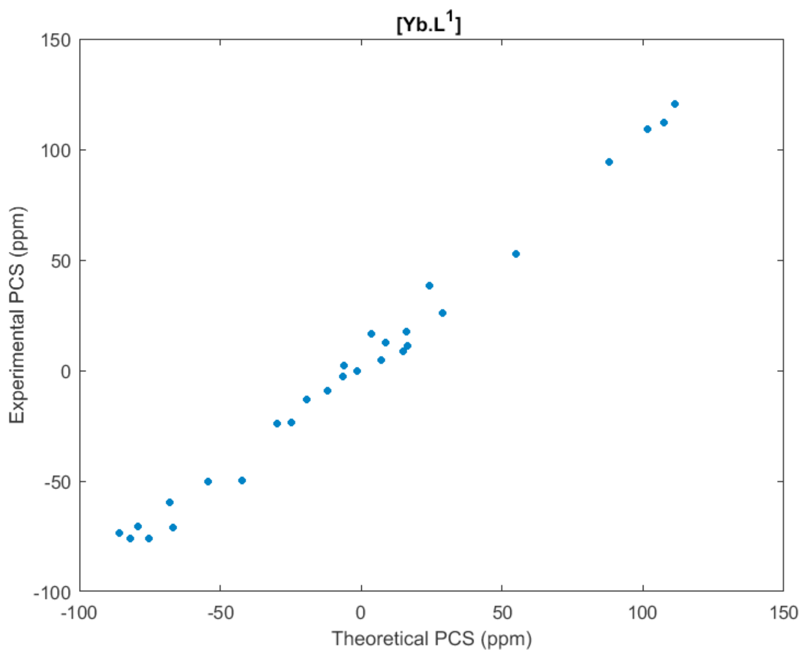

Figure S18. Comparison of the observed and the best fit PCS values for **[Yb.L[1]]**.

Table S4. Traceless part of the magnetic susceptibility tensor (Å^3 in SI units) for **[Yb.L^1]** extracted from the paramagnetic shifts (±0.002 Å^3) using the geometry of Λ-λλλλ conformer and computed by CASSCF (*T*=300.2 K) for various structures. Axiality, rhombicity (Å^3 in SI units) and Euler angles in degrees are shown for convenience.

	fit			Λ-λλλλ			Λ-λλλλ+H_2O			Λ-δδδδ			Λ-δδδδ+H_2O		
$\tilde{\chi}$	-0.028	0.014	-0.000	0.297	0.093	0.028	0.110	-0.027	0.006	0.198	0.072	0.016	0.114	0.037	0.018
	0.014	-0.056	0.009	0.093	0.156	-0.005	-0.027	0.309	-0.026	0.072	0.263	0.002	0.037	0.318	-0.011
	-0.000	0.009	0.084	0.028	-0.005	0.047	0.006	-0.026	0.097	0.016	0.002	0.034	0.018	-0.011	0.081
ax	0.127			0.268			0.215			0.218			0.231		
rh	0.021			0.036			0.007			0.060			0.024		
α	[58 4 54]			[26 86 167]			[98 97 349]			[57 88 354]			[260 88 208]		

Table S5. Optimized geometry (M06-2X/cc-pVDZ SMD(water)) of **[Yb.L^1]** conformers with and without explicit water molecules.

	Λ-λλλλ			Λ-λλλλ+H_2O			Λ-δδδδ			Λ-δδδδ+H_2O		
Yb	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
C	0.6036	-2.9922	-0.7562	0.4335	-2.9843	-0.8650	2.7919	1.3516	-0.6211	1.4613	-2.7929	-0.3932
C	-0.3207	3.0491	-0.7863	-0.3981	3.0969	-0.6875	-2.8824	-1.2097	-0.5986	-1.2907	2.9084	-0.4573
C	-2.9966	-0.4386	-0.8640	-3.0461	-0.4153	-0.7311	1.3129	-2.8159	-0.6334	-2.8397	-1.3713	-0.4828
O	0.8620	-3.9989	-1.4268	0.6126	-3.9702	-1.5878	3.6681	2.0309	-1.1686	2.2394	-3.6548	-0.8220
O	0.9798	-1.7994	-1.0336	0.8158	-1.7881	-1.1348	1.5471	1.3621	-0.9303	1.4369	-1.5697	-0.7739
O	-3.9933	-0.6596	-1.5634	-4.0405	-0.5369	-1.4555	2.0073	-3.6919	-1.1625	-3.7368	-2.0717	-0.9719
O	-0.4029	4.0417	-1.5207	-0.5378	4.1028	-1.3905	-3.8007	-1.7337	-1.2442	-1.9100	3.8158	-1.0267
O	-0.7093	1.8681	-1.0969	-0.7852	1.9137	-1.0079	-1.6396	-1.2682	-0.9049	-1.2976	1.6765	-0.8110
O	-1.7924	-0.7678	-1.1596	-1.8748	-0.8686	-0.9908	1.2822	-1.5839	-0.9859	-1.6024	-1.4242	-0.8010
N	2.0733	0.0000	1.5536	2.0643	0.0000	1.4752	-0.0285	2.0854	1.3986	2.0868	0.0000	1.5266
N	-0.0060	-2.0556	1.4472	-0.0300	-2.0773	1.3915	2.0911	0.0000	1.3696	-0.0131	-2.0809	1.4980
N	-2.0829	-0.0074	1.3899	-2.0618	0.0106	1.4824	0.0273	-2.0915	1.3920	-2.0908	-0.0093	1.4626
N	0.0156	2.0630	1.4591	0.0275	2.0668	1.5167	-2.0900	0.0061	1.4503	0.0171	2.0902	1.5137
N	2.0761	0.8814	-1.0372	2.0473	0.9877	-1.0713	-1.4071	1.7255	-1.0488	1.8377	1.4635	-0.8393
C	1.9138	-1.0143	2.6171	1.9328	-1.0461	2.5135	1.3236	2.2988	1.9754	2.2598	-1.3230	2.1745
C	1.3044	-2.2993	2.0877	1.3132	-2.3187	1.9656	1.9460	0.9984	2.4544	0.9341	-1.9050	2.6190
C	-1.0636	-1.9975	2.4785	-1.0309	-2.0186	2.4782	2.3352	-1.3373	1.9578	-1.3613	-2.3308	2.0513
C	-2.3291	-1.3589	1.9419	-2.3105	-1.3449	2.0238	1.0483	-1.9686	2.4586	-2.0129	-1.0412	2.5219
C	-2.0032	0.9965	2.4689	-1.9526	0.9918	2.5777	-1.3031	-2.3035	2.0055	-2.2861	1.3124	2.0947
C	-1.3528	2.2824	1.9879	-1.3191	2.2830	2.0967	-1.8877	-1.0025	2.5210	-0.9685	1.8653	2.6005
C	0.9703	1.9709	2.5849	1.0178	1.9445	2.6057	-2.3128	1.3252	2.0880	1.3416	2.3259	2.1308
C	2.2788	1.3350	2.1575	2.3071	1.3138	2.1174	-1.0014	1.9624	2.5124	1.9843	1.0281	2.5917
C	-0.2595	-3.1486	0.4962	-0.3398	-3.1612	0.4444	3.2039	0.3762	0.4796	0.4125	-3.1993	0.6422
C	-3.1720	0.3137	0.4556	-3.1733	0.3530	0.5821	0.3630	-3.2123	0.4957	-3.2087	-0.3138	0.5551
C	0.3548	3.1936	0.5779	0.3328	3.2130	0.6484	-3.2501	-0.3689	0.6217	-0.3951	3.2638	0.7252
C	3.2368	-0.3330	0.7164	3.2097	-0.3231	0.5999	-0.3759	3.2395	0.5411	3.2752	0.2539	0.6900
C	3.2651	0.5044	-0.5352	3.2406	0.5939	-0.5926	-1.4647	2.9264	-0.4534	3.0579	1.3681	-0.2937
C	4.4608	0.8474	-1.1563	4.4330	1.0204	-1.1665	-2.4625	3.8457	-0.7732	4.0883	2.2423	-0.6417
C	4.4329	1.6008	-2.3265	4.3958	1.8803	-2.2616	-3.4268	3.5004	-1.7121	3.8407	3.2473	-1.5643
C	3.2084	2.0064	-2.8620	3.1661	2.3161	-2.7606	-3.3676	2.2598	-2.3617	2.5678	3.3735	-2.1388
C	2.0646	1.5953	-2.1748	2.0285	1.8227	-2.1192	-2.3152	1.4248	-1.9942	1.6156	2.4404	-1.7396
C	3.0720	2.8882	-4.0990	3.0067	3.3148	-3.9046	-4.4558	1.7945	-3.3256	2.2508	4.5009	-3.1161
C	2.5972	4.2792	-3.6548	2.5446	4.6548	-3.3097	-3.9907	0.6058	-4.1738	0.8108	4.4212	-3.6269
C	4.4059	3.0238	-4.8350	4.3264	3.5237	-4.6486	-5.6590	1.3522	-2.4760	2.4460	5.8409	-2.3904
C	2.0359	2.2838	-5.0586	1.9485	2.8151	-4.9007	-4.8749	2.9347	-4.2606	3.2095	4.4198	-4.3124
H	1.2686	-0.5869	3.3969	1.3108	-0.6414	3.3229	1.2697	3.0052	2.8216	2.9302	-1.2373	3.0473
H	2.8896	-1.2285	3.0885	2.9213	-1.2752	2.9491	1.9571	2.7684	1.2122	2.7575	-1.9997	1.4682
H	1.9715	-2.7592	1.3450	1.9514	-2.7439	1.1787	2.9319	1.2163	2.9013	1.1131	-2.8733	3.1205
H	1.1988	-3.0306	2.9071	1.2544	-3.0738	2.7685	1.3243	0.5562	3.2443	0.4692	-1.2391	3.3586
H	-0.6769	-1.4155	3.3268	-0.5922	-1.4599	3.3160	3.0556	-1.2700	2.7916	-1.3083	-3.0325	2.9029
H	-1.2897	-3.0094	2.8583	-1.2560	-3.0339	2.8491	2.7950	-1.9731	1.1892	-1.9730	-2.8151	1.2807
H	-2.7488	-1.9859	1.1415	-2.7875	-1.9445	1.2363	1.2725	-2.9629	2.8832	-3.0253	-1.2654	2.9020
H	-3.0926	-1.3142	2.7380	-3.0235	-1.2958	2.8652	0.6282	-1.3617	3.2710	-1.4455	-0.6263	3.3643
H	-1.4250	0.5644	3.2978	-1.3456	0.5448	3.3771	-1.2382	-3.0263	2.8375	-2.9972	1.2423	2.9364
H	-3.0099	1.2223	2.8626	-2.9464	1.2080	3.0086	-1.9657	-2.7438	1.2487	-2.7345	1.9918	1.3575
H	-1.9575	2.7313	1.1870	-1.9502	2.7451	1.3248	-2.8493	-1.2083	3.0226	-1.1493	2.8129	3.1380
H	-1.3247	3.0187	2.8098	-1.2595	3.0034	2.9311	-1.2173	-0.5682	3.2743	-0.5310	1.1623	3.3215
H	0.5024	1.3760	3.3815	0.5767	1.3267	3.3992	-2.9645	1.2254	2.9736	1.2495	3.0011	3.0004
H	1.1649	2.9733	3.0045	1.2331	2.9330	3.0481	-2.8403	1.9702	1.3750	1.9803	2.8367	1.4003
H	2.7821	1.9752	1.4195	2.7902	1.9731	1.3834	-1.2019	2.9567	2.9477	2.9864	1.2479	3.0000
H	2.9559	1.2592	3.0262	3.0120	1.2021	2.9590	-0.5349	1.3571	3.3004	1.3979	0.5995	3.4144
H	-1.3090	-3.1162	0.1658	-1.4076	-3.1290	0.1854	3.5514	-0.5255	-0.0452	-0.4575	-3.5407	0.0628
H	-0.0768	-4.1370	0.9498	-0.1224	-4.1521	0.8769	4.0572	0.7879	1.0432	0.7864	-4.0512	1.2348
H	1.4406	3.2131	0.3921	1.4098	3.2392	0.4190	-3.7184	0.5451	0.2230	0.4961	3.7449	0.2931
H	0.0839	4.1586	1.0375	0.0768	4.1711	1.1311	-4.0224	-0.8932	1.2089	-0.8942	4.0232	1.3501
H	3.1643	-1.3882	0.4165	3.1013	-1.3568	0.2417	0.5205	3.5029	-0.0380	3.4771	-0.6573	0.1100
H	4.1781	-0.2047	1.2784	4.1601	-0.2552	1.1564	-0.6579	4.1124	1.1527	4.1588	0.4667	1.3154

H	5.4071	0.5326	-0.7164	5.3828	0.6882	-0.7478	-2.4933	4.8091	-0.2646	5.0667	2.1356	-0.1737
H	5.3740	1.8789	-2.8012	5.3323	2.2179	-2.7053	-4.2336	4.2020	-1.9293	4.6382	3.9448	-1.8278
H	3.3098	4.7270	-2.9451	3.2945	5.0500	-2.6072	-3.8102	-0.2887	-3.5596	0.0805	4.5029	-2.8071
H	1.6122	4.2235	-3.1692	1.5918	4.5408	-2.7702	-3.0697	0.8430	-4.7283	0.6230	3.4781	-4.1630
H	2.5160	4.9447	-4.5285	2.4006	5.3933	-4.1139	-4.7752	0.3547	-4.9026	0.6289	5.2500	-4.3263
H	4.2740	3.6828	-5.7054	4.1671	4.2224	-5.4828	-6.4854	1.0304	-3.1291	2.2266	6.6743	-3.0753
H	4.7624	2.0473	-5.1985	4.7096	2.5780	-5.0616	-6.0202	2.1750	-1.8400	3.4794	5.9575	-2.0309
H	5.1873	3.4629	-4.1985	5.0989	3.9546	-3.9949	-5.3794	0.5056	-1.8284	1.7686	5.9166	-1.5255
H	1.9662	2.9055	-5.9637	1.8919	3.5072	-5.7543	-5.6487	2.5738	-4.9544	2.9941	5.2354	-5.0195
H	1.0357	2.2486	-4.5997	0.9461	2.7723	-4.4480	-4.0207	3.2935	-4.8549	3.0953	3.4624	-4.8433
H	2.3216	1.2647	-5.3614	2.2035	1.8149	-5.2841	-5.2975	3.7875	-3.7103	4.2589	4.5156	-3.9962
H	1.0755	1.8408	-2.5605	1.0416	2.1274	-2.4597	-2.1875	0.4470	-2.4551	0.6075	2.4723	-2.1504
H	-3.1429	1.3864	0.2099	-3.1379	1.4227	0.3313	-0.5582	-3.5465	-0.0041	-3.4501	0.5947	-0.0162
H	-4.1627	0.0960	0.8872	-4.1532	0.1470	1.0453	0.7781	-4.0693	1.0507	-4.1112	-0.6250	1.1068
O				-0.3756	0.2139	-3.2705				-0.0601	-0.0024	-2.5241
H				0.1576	0.7222	-3.8990				-0.6690	0.7317	-2.7120
H				-0.6875	0.8918	-2.6427				0.7600	0.2396	-2.9817

Structure and analysis of magnetic properties of [Yb.L^2]

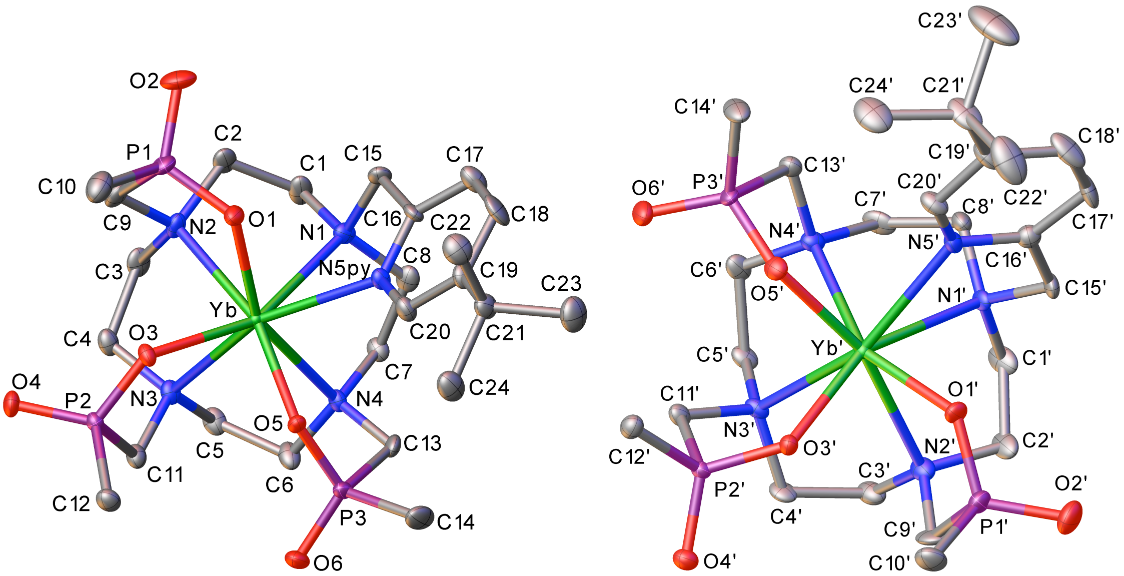

Figure S19. X-ray molecular structure of **[Yb.L^2]**, showing the two independent enantiomeric molecules. Thermal ellipsoids are drawn at the 50% probability level; H atoms are omitted for clarity.

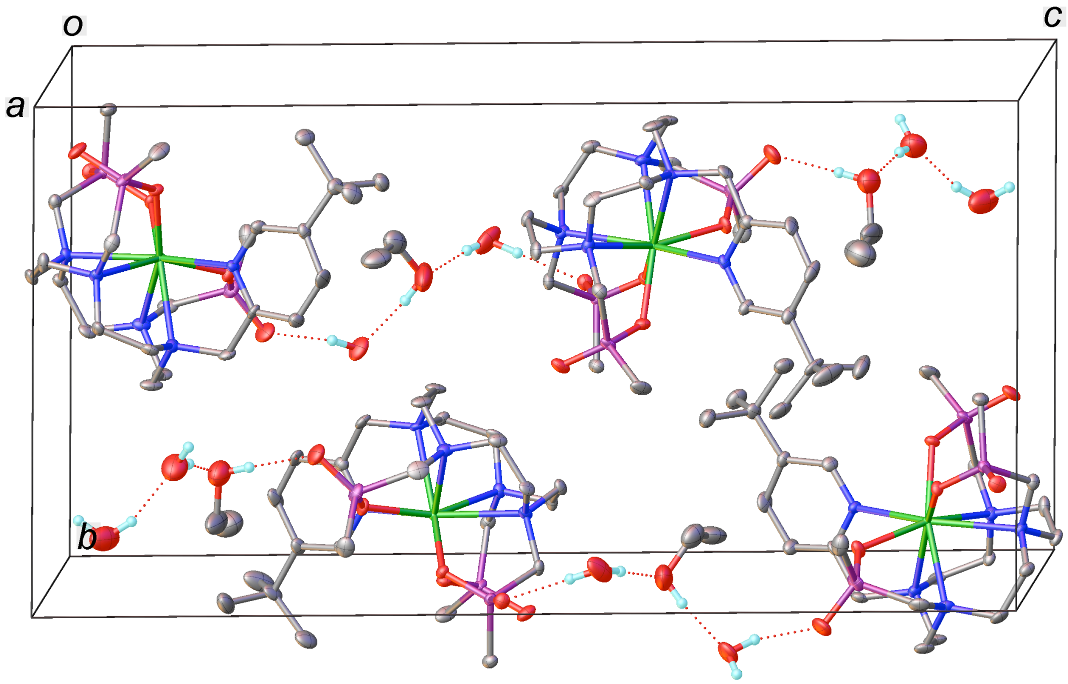

Figure S20. Crystal packing of **[Yb.L²]**, showing hydrogen bonds. H atoms are omitted, except those of hydroxyl groups and water.

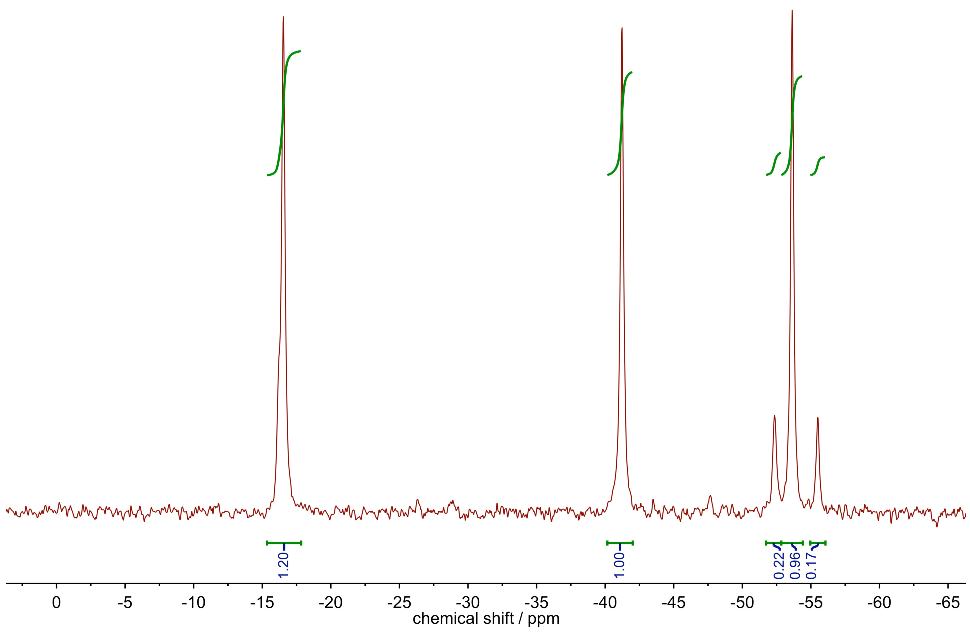

Figure S21. $^{31}P\{^{1}H\}$ NMR spectra of **[Yb.L²]** (9.4 T, D_2O, pD 6, 298 K) showing the major and minor isomers in a 5:1 ratio (the resonance at -16.5 ppm contains overlapping signals).

Table S6. Assigned paramagnetic shifts of major conformer of **[Yb.L²]** protons (4.7 T, D_2O, 295 K) and phosphorus atoms.

Label	Shift, ppm	Width, Hz	R_1, s^{-1}	Diamagnetic reference, ppm
py6	115.60	160	332	8.60
c5ax	115.60	160	332	3.41
c3ax	85.57	137	248	3.41
c7ax	54.18	130	277	3.37
c4eq	50.90	79	101	2.50
c5eq	50.02	64	100	2.31
c1ax	36.30	136	250	3.51
c4ax	33.43	106	270	3.53

c3eq	27.07	72	89	2.40
c6eq	21.09	84	92	2.48
py4	18.98	53	9.8	7.97
tBu	16.33	45	11.1	1.24
a2eq	11.99	63	63	2.59
py3	6.12	47	18	7.35
c7eq	1.92	74	81	2.29
Me3	-9.37	70	42	1.26
Me1	-9.37	70	42	1.26
c6ax	-9.37	70	42	3.53
c2eq	-14.40	54	61	2.59
c8eq	-13.81	66	68	2.43
c1eq	-18.60	81	64	2.47
Me2	-26.27	63	38	1.44
a3eq	-27.00	55	50	2.78
apeq	-28.33	77	50	3.65
a1eq	-28.73	58	54	2.59
a2ax	-38.66	130	183	3.61
a1ax	-40.47	104	149	3.43
c8ax	-30.71	106	186	2.98
a3ax	-49.94	102	172	3.41
apax	-64.10	101	182	4.55
c2ax	-76.41	92	135	3.58
P1	-41.22	-	-	43.90
P2	-16.54	-	-	43.30
P3	-53.64	-	-	41.00

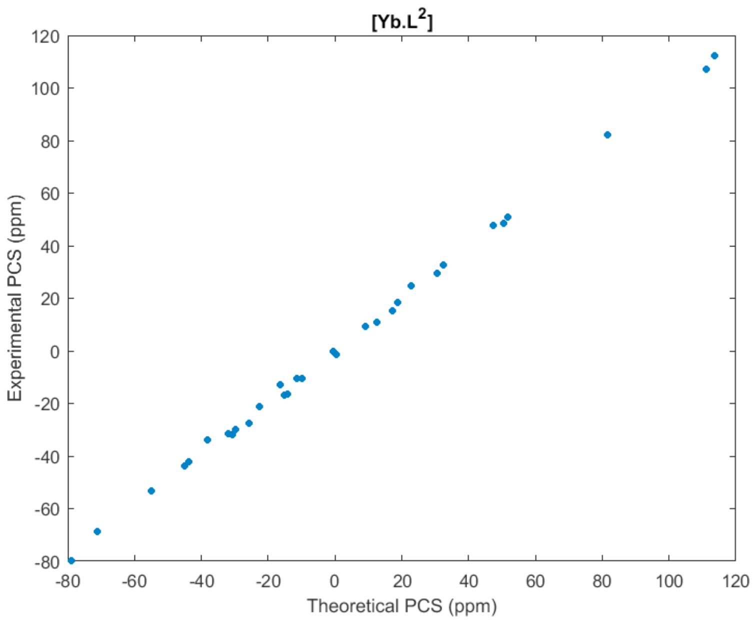

Figure S22. Comparison of the observed and the best fit PCS values for **[Yb.L^2]**.

Table S7. Traceless part of the magnetic susceptibility tensor (Å^3 in SI units) for **[Yb.L^2]** extracted from the paramagnetic shifts (±0.001 Å^3) using the geometry of Λ-λλλλ conformer and computed by CASSCF (T=300.2 K) for various structures. Axiality, rhombicity (Å^3 in SI units) and Euler angles in degrees are shown for convenience.

	fit			**(RRR)-Λ-(λλλλ)**			**(RRR)-Λ-(λλλλ)+H_2O**		
χ	-0.017	0.015	-0.037	0.150	0.026	-0.052	0.140	0.022	-0.043
	0.015	-0.043	0.002	0.026	0.127	-0.017	0.022	0.121	0.009
	-0.037	0.002	0.060	-0.052	-0.017	0.232	-0.043	0.009	0.250
ax	0.113			0.139			0.142		
rh	0.016			0.016			0.024		
α	[185 23 300]			[204 29 111]			[358 161 226]		

Table S8. DFT (M06-2X/cc-pVDZ SMD(water)) optimized geometry of [Yb.L^2] used for the fitting.

Yb	0	0	0
P1	0.71371	-3.23288	-0.85119
P3	-0.84366	3.24873	-0.75455
P2	-3.26175	-0.60269	-0.8145
O	1.97553	-4.09332	-0.70558
O	0.9766	-1.70257	-1.08014
O	-4.12774	-1.86211	-0.68213
O	-2.27852	3.74505	-0.51685
O	-0.73359	1.75095	-1.21041
O	-1.74982	-0.86707	-1.14376
N	2.07533	0	1.44039
N	0.00118	-2.10665	1.53584
N	-2.0512	-0.00842	1.57779
N	-0.02531	2.11508	1.5931
N	2.05264	0.78465	-1.19933
C	-3.95251	0.53649	-2.03803
C	1.96286	-0.97418	2.55136
C	1.35125	-2.29197	2.11461
C	-0.99964	-2.00272	2.61674
C	-2.28533	-1.36416	2.12677
C	-1.89707	0.93252	2.70946
C	-1.32601	2.26839	2.28286
C	1.05757	1.97646	2.58917
C	2.3098	1.35394	2.00061
C	-0.32681	-3.2606	0.67578
C	-3.20552	0.38757	0.74738
C	0.21124	3.3059	0.75655
C	3.23397	-0.35256	0.59914
C	3.23936	0.38599	-0.71574
C	4.41159	0.5638	-1.44296
C	4.33952	1.09297	-2.72953
C	3.10206	1.44675	-3.27429
C	1.99153	1.29059	-2.43744
C	2.91001	1.92224	-4.71354
C	2.11762	3.2361	-4.73925
C	4.25011	2.13875	-5.41803
C	2.1165	0.84376	-5.46924
C	0.00796	4.31959	-1.9354
C	-0.3528	-3.85457	-2.17146
c1ax	1.34179	-0.52203	3.33523
c1eq	2.95806	-1.15757	2.99351
c2ax	1.98737	-2.78464	1.36775
c2eq	1.30494	-2.97304	2.98307
c3ax	-0.5656	-1.40873	3.43167
c3eq	-1.21929	-3.00265	3.03143
c4ax	-2.74583	-1.98239	1.34518
c4eq	-3.01239	-1.31473	2.95744
c5ax	-1.23148	0.46641	3.44844
c5eq	-2.87225	1.09088	3.20422
c6ax	-2.01536	2.78301	1.60246
c6eq	-1.21133	2.91702	3.16979
c7ax	0.68281	1.36343	3.41924
c7eq	1.31408	2.9637	3.01356
c8ax	2.70003	1.98928	1.19304
c8eq	3.09278	1.30543	2.77798
a1ax	-1.37754	-3.18934	0.35996
a1eq	-0.18843	-4.21566	1.21484
a3ax	1.25291	3.30356	0.40186

a3eq	0.04778	4.23989	1.32521
apax	3.18549	-1.42646	0.36552
apeq	4.17769	-0.17106	1.1427
py3	5.36822	0.2652	-1.01389
py4	5.25765	1.21163	-3.30482
tBu	2.63535	4.02414	-4.17062
tBu_1	1.1095	3.10848	-4.32007
tBu_2	2.00602	3.57954	-5.77915
tBu_3	4.06843	2.49567	-6.44243
tBu_4	4.83013	1.20632	-5.48468
tBu_5	4.86246	2.89199	-4.89908
tBu_6	1.95299	1.15847	-6.51168
tBu_7	1.13358	0.67539	-5.00334
tBu_8	2.6628	-0.11179	-5.47675
py6	0.98778	1.56443	-2.76849
Me3	0.01394	5.34587	-1.54113
Me3_1	-0.54388	4.3033	-2.88609
Me3_2	1.03914	3.9765	-2.09368
Me1	-1.23737	-3.21093	-2.26526
Me1_1	-0.6586	-4.88579	-1.94545
Me1_2	0.21616	-3.84715	-3.11212
a2ax	-3.09587	1.44094	0.45047
a2eq	-4.15668	0.28061	1.30133
Me2	-4.96183	0.83692	-1.72202
Me2_1	-4.01689	0.02051	-3.00652
Me2_2	-3.31111	1.4237	-2.12697