ESI for: Magnetism in Ln Molecular Systems with 4f/valence shell interplay (FV-Magnetism)

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Abstract. The hunt for the high-performance single-molecule magnets (SMM) revealed that atomic and molecular lanthanide systems combining 4*f*-shell and valence magnetism (FV-magnetism) may show magnetic bistability up to unexpectedly high temperatures. Here we rationalize the stability of the magnetism in the FV-systems from first principles on the example of $Ln^{II}(Cp^{iPr_5})_2$ molecules.

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1. Additional DFT-based data for the model Ln(Cp^{iPr_5})$_2$ systems

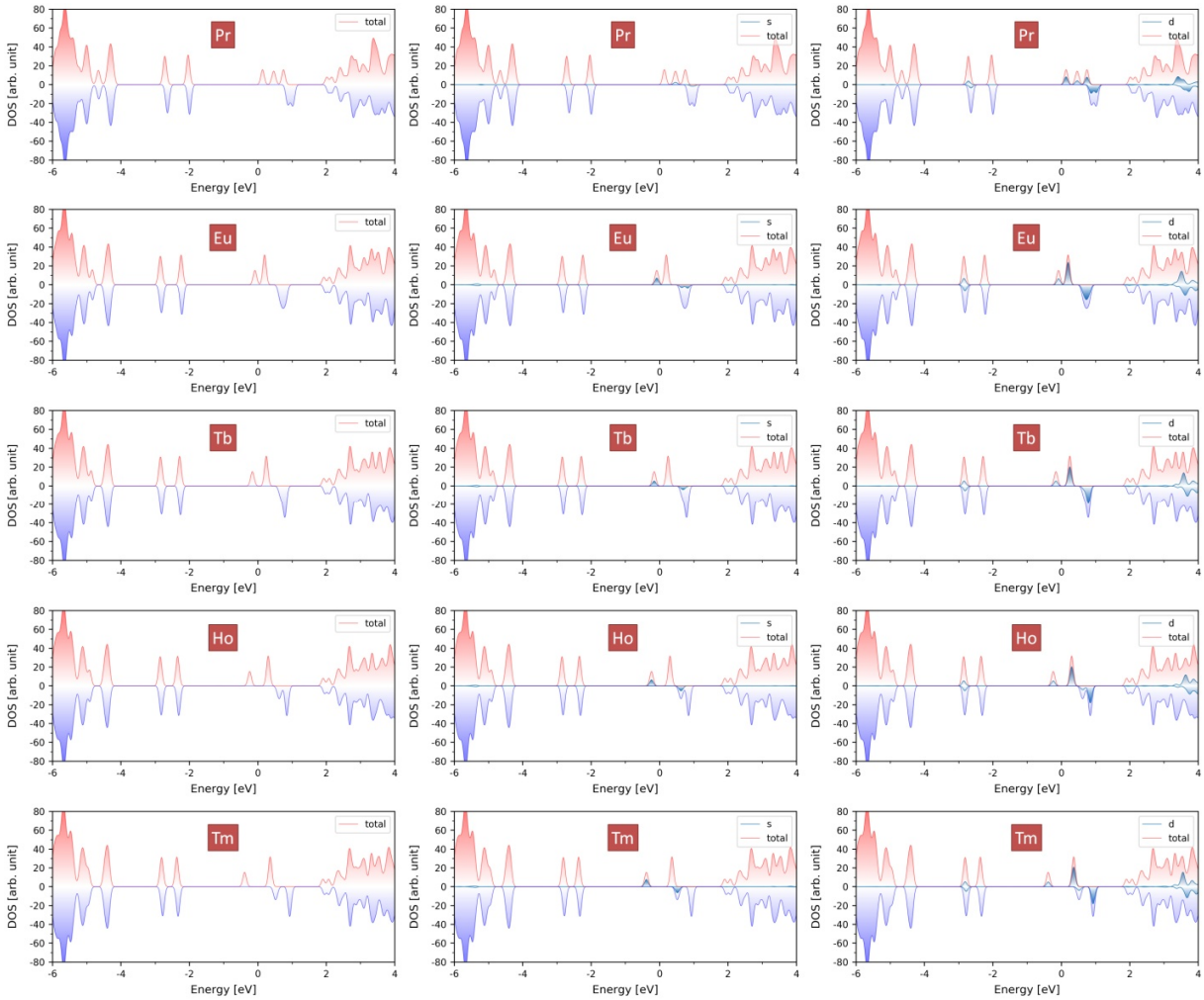

Fig. S1 Total DOS and *s*-/*d*- projected(on Ln) DOS for spin polarised solution of the optimized crystal Ln(Cp^{iPr_5})$_2$. (Ln=Pr-Tm). Well optimized structures in the separate attachment of this ESI (**str.tar**).

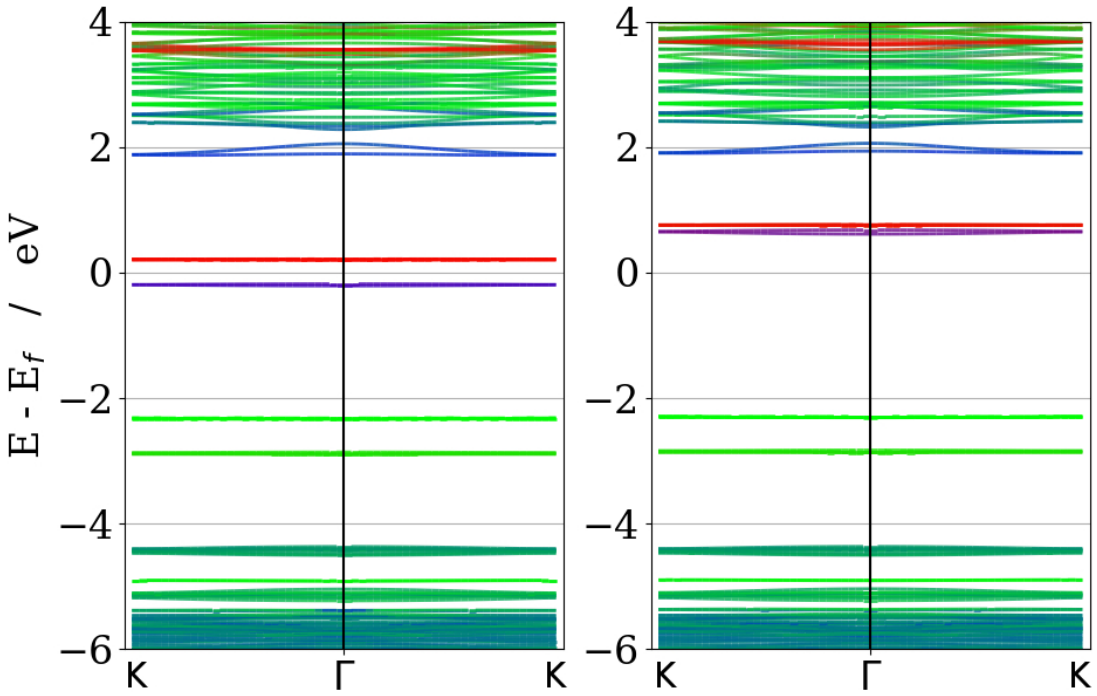

Fig. S2 Spin-up(left) and spin-down(right) K-G-K band structure lines for Tb($\mathrm{Cp}^{i\mathrm{Pr}_5}$)$_2$. Bands are colorized accordingly to the total orbital contributions as follows: red- *d*; blue-s; green-*p*; moments.

2. g_z-*E* tables for SOC-doublets data for Tb(Cp^{iPr_5})$_2$ and q-Ln^{2+}-q model

Tb(Cp^{iPr_5})$_2$

E, cm^{-1}	gx	gy	gz
0.0	0.0014	0.0032	19.9276
48.4	6.5368	11.3905	0.1507
80.0	7.6200	7.2508	3.8891
89.9	0.5150	0.5363	13.7012
101.6	5.4451	7.9548	3.1294
118.9	3.7143	3.3141	8.4808
128.8	5.3942	3.0204	6.0105
166.4	0.9517	1.0428	6.1507
295.4	0.0850	0.0549	8.0695
509.3	0.0266	0.0292	10.8228
772.4	0.0014	0.0075	13.7826

q-Tb^{2+}-q, q=-1.03

E, cm^{-1}	gx	gy	gz
0.0	0.0000	0.0000	19.9816
61.2	10.1943	10.1943	2.0069
74.6	0.0000	0.0000	6.0022
118.6	0.0000	0.0000	9.7443
177.3	0.0000	0.0000	16.1926
196.3	9.9455	9.9455	1.0399
196.6	0.0000	0.0000	3.2398
207.3	0.0000	0.0000	5.8950
225.4	0.0000	0.0000	8.7034
238.4	0.0000	0.0000	12.3391
259.7	0.0000	0.0000	13.4301
743.4	0.0000	0.0000	15.8946

q-Gd^{2+}-q, q=-1.5

E, cm^{-1}	gx	gy	gz
0.7	0.0000	0.0000	4.0046
2.7	0.0000	0.0000	8.0092
6.1	0.0000	0.0000	12.0136

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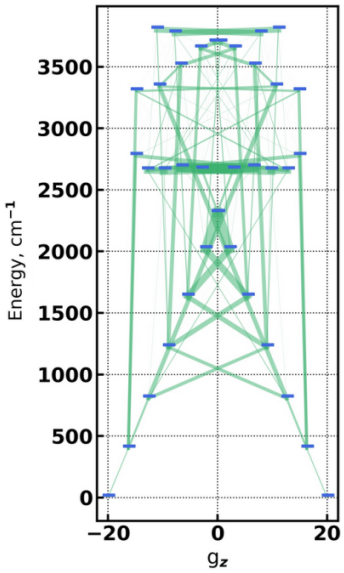
q-Tb^{2+}-q, q=-1.5

E, cm^{-1}	gx	gy	gz
0.0	0.0000	0.0000	20.0150
397.8	0.0000	0.0000	16.2917
806.0	0.0000	0.0000	12.6087
1220.7	0.0000	0.0000	8.9862
1632.3	0.0000	0.0000	5.4699
2017.7	0.0000	0.0000	2.2009
2311.5	8.4961	8.4961	0.0919
2657.9	0.0000	0.0000	9.7582
2658.5	0.0000	0.0000	12.7990
2665.5	8.2612	8.2612	2.8722
2683.0	0.0000	0.0000	6.5451



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q-Dy^{2+}-q, q=-1.5

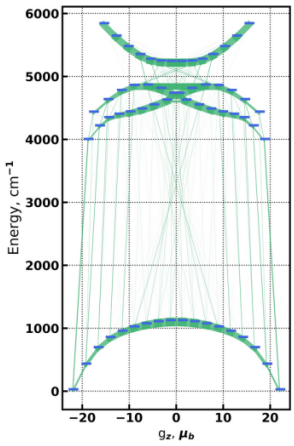
E, cm^{-1}	gx	gy	gz
0.0	0.0000	0.0000	22.0131
735.2	0.0000	0.0000	18.6690
1411.9	0.0000	0.0000	15.5717

$[Tb(Cp^{iPr_5})_2.]^+$

E, cm^{-1}	gx	gy	gz
0.0	0.0000	0.0000	18.0117
250.49/250.50	0.0000	0.0000	14.6918
523.41/523.41	0.0000	0.0000	11.3783
782.11/782.15	0.0000	0.0000	8.2532
981.05/981.60	0.0000	0.0000	-

q-Ho^{2+}-q, q=-1.5

E, cm^{-1}	gx	gy	gz
0.0	0.0000	0.0000	22.0111
408.9	0.0000	0.0000	19.2601
671.3	0.0000	0.0000	16.6571
831.7	0.0000	0.0000	14.1022
932.4	0.0000	0.0000	11.5474
1000.4	0.0000	0.0000	8.9829
1048.8	0.0000	0.0000	6.4137
1081.5	0.0000	0.0000	3.8456
1098.4	11.5985	11.5985	1.2813

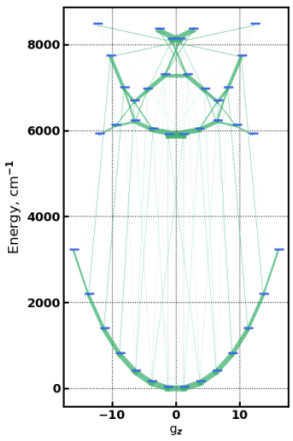


q-Er^{2+}-q, q=-1.5

E, cm^{-1}	gx	gy	gz
0.0	0.0000	0.0000	2.5227
14.6	0.0000	0.0000	5.0420
57.7	0.0000	0.0000	7.5569
128.1	0.0000	0.0000	10.0701
226.7	0.0000	0.0000	12.5850
361.6	0.0000	0.0000	15.0985
555.2	0.0000	0.0000	17.5893
854.1	0.0000	0.0000	20.0090

q-Tm^{2+}-q, q=-1.5

E, cm^{-1}	gx	gy	gz
0.0	8.5081	8.5081	1.2664
122.6	0.0000	0.0000	3.7967
378.6	0.0000	0.0000	6.3161
786.7	0.0000	0.0000	8.8105
1370.4	0.0000	0.0000	11.2666
2161.3	0.0000	0.0000	13.6698
3196.1	0.0000	0.0000	16.0065



The list of first 30 SOC-doublets for non-Kramers systems:

q-Dy^{2+}-q, q=-1.5			q-Er^{2+}-q, q=-1.5		
id	**Energy, cm-1**	**J**	**id**	**Energy, cm-1**	**J**
1	0.0	8.1	1	0.0	8
2	0.0	8.1	2	14.6	8
3	735.3	8	3	14.6	8
4	735.3	8	4	57.7	8
5	1412.0	8	5	57.7	8
6	1412.0	8	6	128.1	8
7	1937.3	8	7	128.1	8
8	1937.3	8	8	226.7	8
9	1997.9	8	9	226.7	8
10	2024.8	8	10	361.6	8.1
11	2024.8	8	11	361.6	8.1
12	2097.5	8	12	555.2	8.1
13	2097.5	8	13	555.2	8.1
14	2182.5	8	14	854.1	8.1
15	2182.5	8	15	854.1	8.1
16	2183.9	8	16	1345.6	8.1
17	2183.9	8	17	1345.6	8.1
18	3458.1	7.2	18	4907.5	7.1
19	3458.1	7.2	19	4923.2	7.1
20	3757.4	7	20	4923.2	7.1
21	3757.4	7	21	4971.4	7.1
22	3772.4	7	22	4971.4	7.1
23	3772.4	7	23	5055.1	7.1
24	3838.4	7.1	24	5055.1	7.1
25	3838.4	7.1	25	5064.9	6.5
26	3983.8	7.2	26	5064.9	6.5
27	3983.8	7.2	27	5104.8	6.3
28	4012.6	7.4	28	5104.8	6.3
29	4025.9	7.4	29	5142.3	6.9
30	4025.9	7.4	30	5142.3	6.9

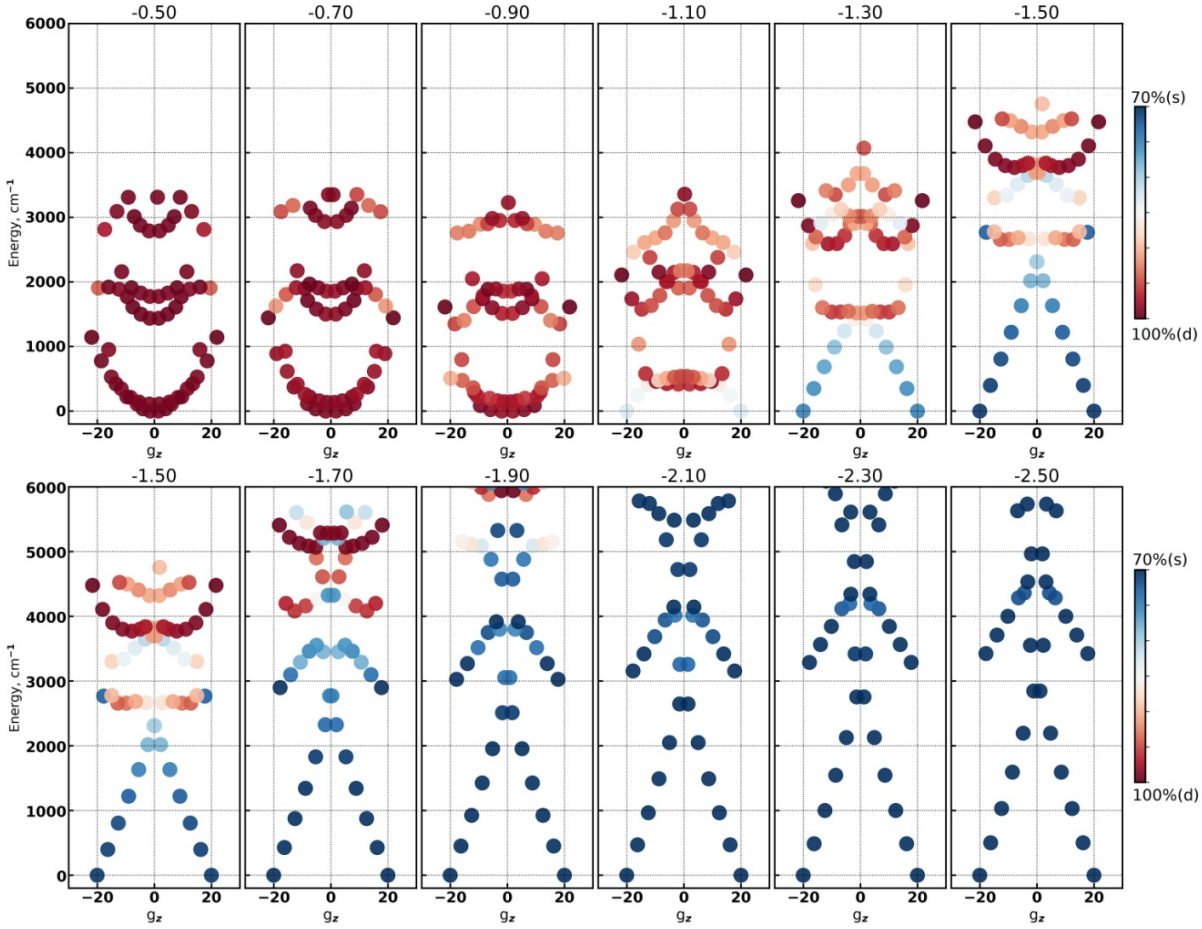


Fig. S3 *Ab initio* g_z-E diagram for SOC-doublets computed at RASSCF/RASSI/SO level colorized with valence shell contribution for q-Tb^{+2}-q model geometry where q ∈[-0.5,-2] with step 0.2.