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Supplementary Information

Unprecedented Magnetic Relaxation via Fourth Excited State in Low-Coordinate Lanthanide Single-ion Magnets: A Theoretical Perspective

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Computational Details:

Here we have performed all the *ab initio* calculations using MOLCAS 7.8[1-3] suite. We have employed [ANO-RCC[4]... 8s7p5d3f2g1h.] basis set for Er and Dy, [ANO-RCC...3s2p.] basis set for C, [ANO-RCC...2s.] basis set for H, [Si.ANO-RCC...4s3p1d.] basis set for Si, [ANO-RCC...3s2p1d.] basis set for N, and [ANO-RCC...3s2p1d.] basis set for O atoms. The ground state f- electron configuration for Er(III) is $4f^{11}$ and this yields $^4I_{15/2}$ as the multiplet ground state. First we have performed CASSCF[5] calculations with an active space of eleven active electrons in seven 4f orbitals (11,7). With this active space, we have computed 35 quartets as well 112 doublet states in the CI (Configuration Interaction) procedure. After computing these excited states, we have mixed all these 35 quartets and 112 doublets using RASSI-SO[5] module to compute the spin-orbit coupled states. For Dy(III) ion the f-electron configuration is $4f^9$ which yields the $^6H_{15/2}$ as the multiplet for the ground state. The CASSCF calculations have been performed with an active space of nine active electrons in seven 4f orbitals (9,7). Here we have computed only 21 roots as it found to be the robust towards computing the g-tensors for Dy(III) ions. [6] We have mixed these 21 roots in the RASSI-SO module to compute the spin-orbit coupled states. The computed SO states of Dy(III) and Er(III) have been taken into the SINGLE_ANISO code to compute the g-tensors. In order check the effects of higher excited states (quartets and doublets) on the magnetic anisotropy and low-lying energy spectrum, we have also performed RASSI calculations by mixing 21 sextets, 108 quartets and 32 doublets which lie within an energy window of 40,000 cm^{-1}. The obtained low-lying energy spectrum for Dy(III) complexes by mixing 21 sextets, 108 quartets and 32 doublets is similar to the pattern computed with 21 roots only. The Er(III) and Dy(III) ion has eight low-lying Kramers doublets for which the anisotropic g-tensors have been computed. The Cholesky decomposition for two electron integrals is employed throughout our calculations. Using SINGLE_ANISO code we have also extracted the crystal field parameters as implemented in MOLCAS 7.8. The transition matrix elements are computed using a MOLCAS routine provided by Prof. L. Chibotaru, University of Leuven, Belgium. Mulliken charges and the spin densities have been computed using DFT calculations employing Gaussian 09 [7] suite. Here we have employed the B3LYP[8-11] functional along with the Cundari-Stevens double ζ polarization basis set[12] for the Er(III) and Dy(III) ions and the Ahlrichs triple ζ basis set[13] has been employed for rest of the atoms.

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Table S1. CASSCF+RASSI computed spin-free and spin-orbit state energies for complex **1a**.

Spin-free Energies for complex 1a		Spin-Orbit Energies for complex 1a	
0.000	43934.212	0	40675.988
1.905	43934.890	101.38	40707.580
114.498	43945.027	189.099	40794.364
115.913	44035.637	266.348	40820.240
199.407	44038.468	331.057	40922.260
201.449	44095.317	439.920	40957.915
255.025	44102.786	500.341	41132.594
362.956	44116.938	539.265	41238.031
418.668	44457.552	6586.831	41409.026
419.312	44459.734	6690.044	41475.452
507.985	44932.169	6784.476	41499.085
509.545	44932.218	6867.725	49828.104
549.466	45318.425	6950.641	49912.136
18159.747	45318.610	7008.365	49922.350
18198.349	45606.118	7042.185	49973.788
18202.896	45624.927	10662.412	50051.859
18325.613	45824.530	10760.809	50103.022
18331.274	45826.674	10847.663	50158.803
18408.861	45945.021	10922.538	50231.318
18697.368	45956.089	10974.997	50272.950
18771.690	45992.109	11003.966	50324.127
28654.535	49986.204	13488.964	50640.703
28654.633	49986.458	13563.412	50884.686
28689.993	50150.383	13660.075	50898.068
28852.159	50150.879	13729.395	51065.357
28859.638	50230.820	13785.355	51177.134
28907.634	50271.184	18975.215	51233.305
28910.753	50323.347	19013.594	51587.128
28913.309	50323.664	19097.115	51674.552
28960.402	50375.691	19244.677	51918.701
46169.495	50379.700	19485.735	52059.930
46174.529	50404.166	22771.147	52160.358
47382.562	50892.302	22794.846	52221.831
47394.820	50894.843	22822.759	52335.928
47686.310	51773.978	22872.712	52467.804
18061.192	51777.837	22876.710	52560.412
18069.382	52075.369	22894.336	52610.927
18070.137	60479.116	23624.471	54719.019
18100.844	60509.007	23823.511	54841.225
18101.063	60796.765	25136.101	55075.148
18145.316	60798.514	25206.502	55700.448
18156.351	60904.547	25342.509	56233.164
18209.670	60905.390	25568.021	56668.279
18209.705	60924.950	27274.133	57012.595
18271.385	76646.242	27290.760	57271.515
18271.484	76646.379	27463.566	57442.979
23773.668	77020.401	27532.699	57528.918
23825.368	77078.507	27870.457	58515.788
23828.031	77356.030	27897.158	58644.712
23970.734	77357.719	27927.637	58732.518
23971.185	77537.362	27937.895	58796.825

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24172.695	77542.530	27998.165	58839.750
24179.214	77598.205	28084.939	59422.762
24403.929	109235.713	31416.541	60616.872
24403.982	109339.012	31709.924	60740.154
26371.490	110577.403	31991.411	61018.494
26371.493	110578.961	32252.297	61209.661
26685.071	111276.989	32472.064	61260.175
26685.869	111292.378	32638.683	61344.420
26988.713	111515.614	32731.989	61434.758
26988.728		32759.719	61479.508
27262.236		32873.642	61666.139
27262.389		32894.293	66743.437
27480.954		32908.336	67086.756
27495.472		32997.946	67264.801
27652.931		33012.203	67357.264
27655.855		33024.843	67510.541
27752.001		33309.402	67696.305
27757.554		33343.453	75981.079
27788.243		33410.540	76241.663
32768.138		33481.771	76274.706
32768.200		34066.071	82823.157
32807.523		34096.640	83188.895
33018.963		34126.482	83426.402
33526.883		34132.366	83544.720
33527.785		34151.907	86607.980
33629.321		37041.866	87006.242
33630.269		37348.162	87320.493
43278.916		37636.767	87527.943
43278.931		37650.401	87631.056
43452.264		37897.803	115598.668
43452.568		38108.123	116854.966
43653.289		38153.110	117429.296
43653.487		38258.326	119778.307
43750.182		38324.838	120991.137
43750.374		40411.961	121709.418
43914.763		40652.445	122056.839

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Table S2. CASSCF+RASSI computed spin-free and spin-orbit state energies for complex **1b** using only 21 roots.

Spin-free Energies for complex 1b	Spin-Orbit Energies for complex 1b	
0.000	0.000	10048.448
51.105	48.452	10086.009
54.161	147.431	10090.452
232.774	304.564	10107.756
237.643	519.201	10530.901
559.677	789.584	10989.119
622.866	1078.226	11409.392
1036.934	1337.275	12004.392
1037.280	3059.197	12076.334
1421.912	3118.493	12111.839
1422.059	3232.180	12168.038
7812.108	3398.639	12222.906
7861.948	3611.688	12252.158
8130.437	3872.587	13899.548
8132.173	4180.183	13933.330
8200.328	5706.077	13949.958
8201.075	5770.194	14008.965
8223.877	5891.241	15314.142
34792.000	6070.693	15314.556
34794.505	6311.950	15376.386
36349.830	6652.584	16292.178
	7924.971	16367.192
	7996.222	16944.687
	8146.109	38678.513
	8383.681	38905.509
	8764.167	39129.468
	9690.124	39307.111
	9758.116	40107.145
	9802.820	40397.392
	9906.016	41393.792
	9989.730	41826.425
		41939.140

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Table S3. CASSCF+RASSI computed spin-free and spin-orbit state energies for complex **2a**.

Spin-free Energies for complex 2a		Spin-Orbit Energies for complex 2a	
0.000	43884.505	0.00	
29.900	43932.433	76.317	41375.891
61.884	43943.655	114.850	41968.725
156.041	44037.356	200.849	42057.135
168.708	44041.065	249.748	42162.475
231.473	44108.594	260.975	49361.567
296.579	44109.265	318.083	49361.567
314.059	44391.593	372.556	49592.538
341.216	44391.745	6609.598	49711.833
358.402	44538.033	6673.879	49858.925
376.693	44538.893	6715.070	49913.185
428.815	44651.745	6766.662	49934.813
454.956	44654.436	6792.336	49982.172
18192.877	44752.449	6808.530	50029.384
18220.323	44767.757	6866.879	50051.678
18303.044	44840.018	10666.862	50088.286
18377.293	44889.546	10719.903	50119.420
18400.803	44922.881	10757.544	50139.564
18448.827	45042.095	10784.907	50220.701
18531.731	45050.200	10796.477	50307.830
18547.141	45241.502	10844.067	50431.113
28547.012	45242.456	13407.675	50586.284
28609.873	45454.859	13515.391	50766.930
28647.735	45454.923	13562.783	50951.211
28683.660	50049.980	13608.609	51299.516
28735.206	50064.446	13642.926	51442.757
28804.362	50080.856	18960.953	51630.817
28837.752	50089.068	19036.375	51832.687
28943.106	50124.986	19101.209	51847.879
28961.733	50147.800	19155.537	51856.413
46505.496	50196.011	19192.191	51902.457
46694.959	50233.586	22652.409	52016.421
46848.277	50241.881	22692.582	52103.570
47096.429	50261.081	22709.912	52174.766
47288.990	50271.767	22739.569	52223.574
18041.694	51225.129	22761.608	54599.670
18045.406	51270.033	22777.435	54668.384
18090.025	51427.447	23594.616	56020.004
18100.422	51644.886	23673.584	56178.563
18118.899	51661.067	25135.882	56297.026
18119.288	60590.583	25199.508	56397.338
18137.133	60608.690	25276.497	56507.087
18151.164	60684.416	25335.695	56661.819
18157.496	60697.955	27252.937	56858.190
18169.423	60717.351	27270.059	57073.699
18174.354	60744.316	27345.128	58502.220
23875.245	60775.294	27556.105	58519.397
23878.287	76924.777	27676.807	58574.585
23973.523	76930.141	27793.677	58634.676
23986.211	77064.389	27821.320	58665.145

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24013.276	77085.054	27869.703	59284.394
24035.223	77118.364	27920.093	60857.046
24073.973	77170.898	27952.331	60921.089
24147.268	77179.837	31815.913	60937.536
24152.937	77340.343	31979.870	61000.274
26837.008	77346.068	32042.706	61038.904
26837.418	110031.768	32117.056	61079.417
26998.649	110061.218	32204.144	61171.327
27007.185	110219.549	32239.583	61239.010
27058.145	110461.068	32369.909	61251.783
27089.627	110568.468	32514.542	66869.625
27123.833	110934.020	32704.716	67088.272
27197.187	110991.916	32753.724	67159.450
27206.554		32771.259	67206.145
27245.867		32844.636	67258.497
27249.432		32883.925	67311.168
27371.878		32911.574	75987.028
27372.122		33208.161	76040.151
27521.868		33255.923	76066.639
27521.981		33273.685	82946.685
32984.328		33305.795	83073.976
33004.060		33954.798	83131.620
33023.328		33962.456	83255.656
33086.476		33975.368	86868.337
33274.058		33984.254	86998.949
33331.703		34018.540	87068.012
33335.677		37372.917	87154.023
33364.461		37531.368	87313.511
43687.653		37593.416	116136.233
43696.879		40780.644	116439.472
43785.543		40827.251	116897.769
43793.697		40870.141	120550.096
43810.109		40983.091	120766.599
43820.832		41260.631	121102.996
		41314.840	121507.797

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Table S4. CASSCF+RASSI computed spin-free and spin-orbit state energies for complex **2b** using only 21 roots.

Spin-free Energies for complex 2b	Spin-Orbit Energies for complex 2b	
0.000	0.000	9915.034
8.841	199.256	9936.955
314.200	377.733	9989.357
329.396	409.488	10094.943
431.170	464.093	11100.802
439.899	525.757	11301.260
537.975	580.878	11513.026
597.428	790.922	11959.006
614.620	3101.076	11993.435
821.128	3247.539	12029.829
821.558	3339.292	12053.357
7742.337	3397.397	12083.609
7772.427	3441.781	13731.994
7832.546	3517.577	13795.645
7882.830	3657.355	13827.832
7976.296	5731.632	13847.018
7999.589	5852.500	15148.125
8039.513	5930.218	15187.690
34704.105	5990.658	15215.007
35186.413	6060.520	16161.004
35485.750	6165.112	16189.541
	7941.677	16772.778
	8044.854	38834.218
	8135.474	38920.160
	8211.540	39018.914
	8304.602	39257.670
	9712.727	40250.615
	9760.015	40457.273
	9778.190	40691.358
	9806.664	41433.976
	9835.138	41520.823
	9860.675	

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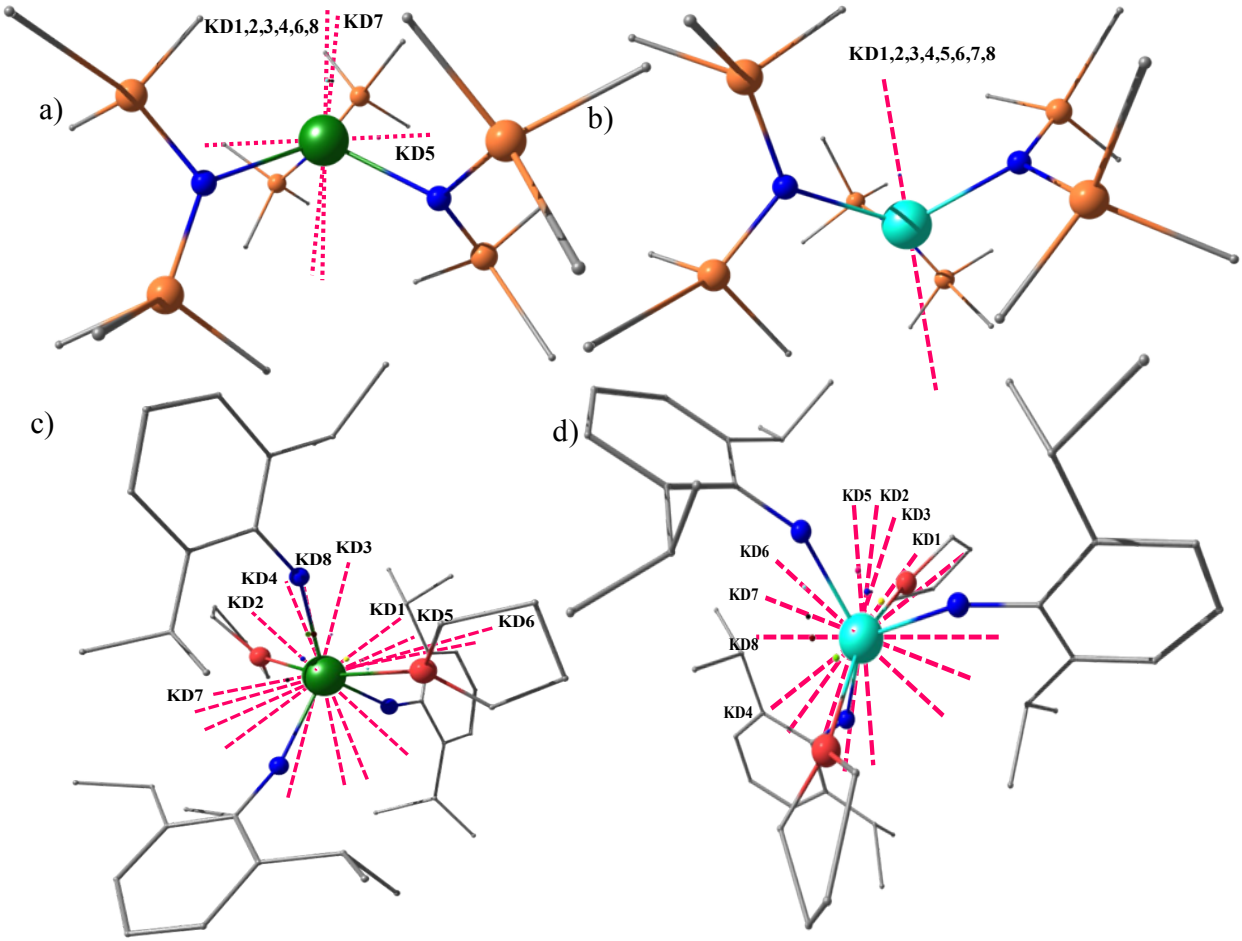

Figure S1. *Ab-initio* computed orientation of principal magnetization axes of the all the KDs for complexes a) **1a** b) **1b** c) **2a** and d) **2b** Color Code: green (Er), cyan (Dy), blue (N), red (O), orange (Si), grey for (C). The hydrogens are omitted for clarity.

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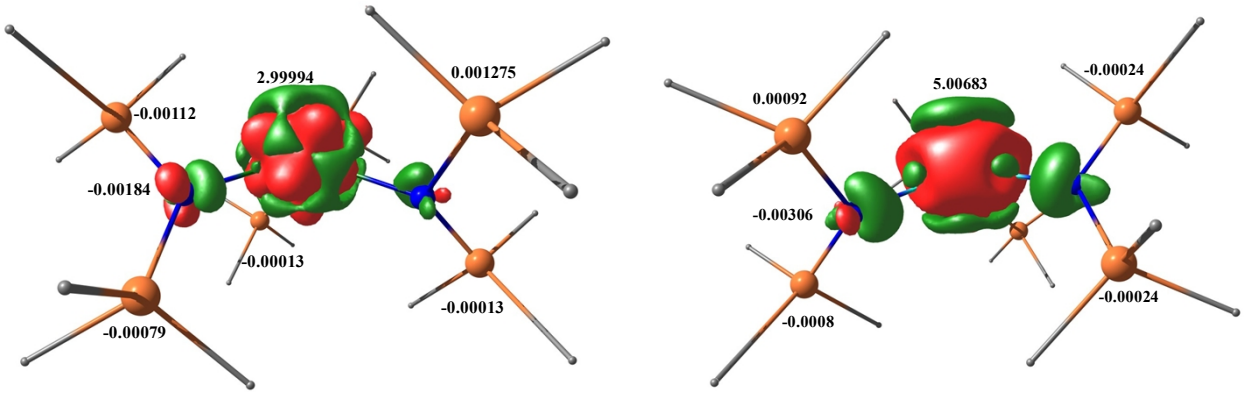

(a) (b)

Figure S2. Spin Density plots of complex (a) **1a** and (b) **1b.** The isodensity surface represented here corresponds to value of $0.005e^{-}/bohr^{3}$. The red and green regions are the positive and negative spin density respectively.

Table S5. SINGLE_ANISO computed g-tensors and relative energies of eight low lying Kramers doublets as well the orbital magnetic moment $<L_z>$ component associated with each KDs for complex **1a** along with the deviation from the principal magnetization axes of first KD. The sign of product of $g_x.g_y.g_z$ also provide for each Kramers Doublet.

KDs Energy(cm^{-1})	g_{xx}	g_{yy}	g_{zz}	$<L_z>$	θ	***Sign of $g_x.g_y.g_z$***
0.000	0.00	0.00	17.88	5.99	0	+
101.38	0.13	0.13	15.48	5.19	0.074	+
180.10	0.06	0.19	12.82	4.30	0.490	-
266.35	0.08	0.22	9.92	3.34	0.335	+
331.06	5.75	5.97	6.30	2.10	79.57	+
439.92	6.12	6.03	3.51	1.19	1.294	-
500.34	0.21	0.42	3.97	1.34	4.469	+
539.27	9.74	8.99	1.05	0.36	0.705	+

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Table S6. SINGLE_ANISO computed g-tensors and relative energies of eight low lying Kramers doublets as well the orbital magnetic moment $<L_z>$ component associated with each KDs for complex **1b** along with the deviation from the principal magnetization axes of first KD. The sign of product of $g_x.g_y.g_z$ also provide for each Kramers Doublet.

KDs Energy(cm^{-1})	g_{xx}	g_{yy}	g_{zz}	$<L_z>$	θ	***Sign of $g_x.g_y.g_z$***
0.000	10.98	10.32	1.38	0.31	0	+
48.45	0.10	0.55	4.19	0.94	0.693	+
147.43	1.29	1.73	6.82	1.54	0.379	-
304.56	1.48	1.49	9.54	2.17	0.274	+
519.20	0.00	0.00	12.26	2.84	0.151	+
789.58	0.01	0.01	14.78	3.52	0.125	-
1078.23	0.01	0.01	17.31	4.24	0.100	+
1337.28	0	0	19.87	2.49	0.090	+

Table S7. SINGLE_ANISO computed g-tensors and relative energies of eight low lying Kramers doublets as well the orbital magnetic moment $<L_z>$ component associated with each KDs for complex **2a** along with the deviation from the principal magnetization axes of first KD. The sign of product of $g_x.g_y.g_z$ also provide for each Kramers Doublet.

KDs Energy(cm^{-1})	g_{xx}	g_{yy}	g_{zz}	$<L_z>$	θ	***Sign of $g_x.g_y.g_z$***
0.000	0.04	0.64	16.20	5.43	0	+
76.32	3.56	5.49	9.97	3.33	55.39	+
114.85	0.29	3.08	9.22	3.06	87.54	+
200.85	0.37	2.45	12.02	4.01	93.93	+
249.75	0.25	4.54	10.67	3.57	25.77	-
260.98	0.25	3.53	11.42	3.83	35.87	-
318.08	0.02	0.68	15.61	5.24	84.54	-
372.56	0.09	0.17	16.82	5.64	94.93	-

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Table S8. SINGLE_ANISO computed g-tensors and relative energies of eight low lying Kramers doublets as well the orbital magnetic moment $<L_z>$ component associated with each KDs for complex **2b** along with the deviation from the principal magnetization axes of first KD. The sign of product of $g_x.g_y.g_z$ also provide for each Kramers Doublet.

KDs Energy(cm^{-1})	g_{xx}	g_{yy}	g_{zz}	$<L_z>$	θ	***Sign of $g_x.g_y.g_z$***
0.000	0.00	0.01	19.67	4.90	0	+
199.26	0.06	0.07	17.15	4.35	18.67	+
377.73	0.29	0.44	14.68	3.78	7.03	+
409.49	0.67	0.88	19.21	4.78	74.10	+
464.09	55.1	6.65	9.14	2.29	48.52	+
525.76	0.92	1.34	13.32	3.29	72.78	+
580.88	0.47	0.92	16.88	4.17	50.89	+
790.92	0	0	19.89	4.95	74.04	+

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Table S9. SINGLE_ANISO computed crystal field parameters for complex **1a**. The major components in the Table are in the bold font. The crystal field Hamiltonian parameter:

$$\hat{H}_{CF} = \sum \sum_{k=-q}^{q} B_q^k \hat{O}_q^k$$

Where B_q^k the crystal is field parameter and O_q^k is the extended Stevens operator. Quantization axis is chosen to be the main magnetic axes of the ground Kramer Doublet.

k	q	B_q^k	B_q^k	B_q^k	B_q^k
		Complex **1a**	Complex **1b**	Complex **2a**	Complex **2b**
2	-2	0.02587	-0.0042	-1.02196	-2.20342
	-1	0.05178	-0.06762	0.4811	2.70427
	0	**-2.99629**	**8.09015**	**-0.9781**	**-3.22959**
	1	0.02321	0.02452	0.02451	**-0.5064**
	2	-0.02654	-0.01981	0.56444	-0.23786
4	-4	-8.84486 x 10^{-5}	-1.54525x 10^{-4}	-0.00581	-0.00565
	-3	-0.03937	0.01748	-0.00487	-0.00827
	-2	1.21293 x 10^{-4}	3.23672 x 10^{-4}	-0.00969	0.01433
	-1	-2.24696 x 10^{-4}	1.72702 x 10^{-4}	0.00978	-0.01681
	0	0.00129	**-0.00237**	**-0.00147**	**-0.00347**
	1	-6.88823 x 10^{-5}	-4.50248 x 10^{-5}	0.00883	**0.00638**
	2	-2.8973 x 10^{-4}	-3.46259 x 10^{-5}	-3.92465 x 10^{-4}	0.02529
	3	**-0.05335**	-0.10277	0.04704	**0.01232**
	4	2.56318 x 10^{-4}	-2.36646 x 10^{-5}	-0.02183	-0.02371
6	-6	1.74789 x 10^{-4}	1.08415 x 10^{-4}	-1.65756 x 10^{-4}	1.24124 x 10^{-4}
	-5	1.36916 x 10^{-5}	-3.98333 x 10^{-6}	**0.00183**	-1.99833 x 10^{-4}
	-4	-1.57799 x 10^{-5}	8.55487 x 10^{-6}	-1.18506 x 10^{-5}	1.92202 x 10^{-5}
	-3	2.17809 x 10^{-4}	1.78278 x 10^{-4}	-1.20382 x 10^{-4}	-1.86489 x 10^{-4}
	-2	-4.70489 x 10^{-6}	8.17853 x 10^{-6}	-2.30679 x 10^{-4}	-3.42703 x 10^{-5}
	-1	1.21298 x 10^{-6}	4.83423 x 10^{-6}	-1.61431 x 10^{-4}	-1.72086 x 10^{-4}
	0	-1.12061 x 10^{-6}	**-1.08768** x 10^{-5}	-3.27297 x 10^{-5}	-4.30435 x 10^{-6}
	1	3.97149 x 10^{-7}	-1.69904 x 10^{-6}	-2.12929 x 10^{-4}	**-6.40945** x 10^{-5}
	2	7.64881 x 10^{-6}	-2.72775 x 10^{-6}	4.1438 x 10^{-5}	1.11622 x 10^{-4}
	3	4.62887 x 10^{-4}	-4.3029 x 10^{-4}	8.71018 x 10^{-5}	-8.11151 x 10^{-5}
	4	8.74372 x 10^{-6}	4.43644 x 10^{-6}	1.49989 x 10^{-4}	-6.06147 x 10^{-5}
	5	-1.01248 x 10^{-7}	2.80239 x 10^{-6}	5.04382 x 10^{-4}	**3.36976** x 10^{-4}
	6	-2.45059 x 10^{-4}	6.3186 x 10^{-5}	7.53159 x 10^{-5}	8.18858 x 10^{-5}

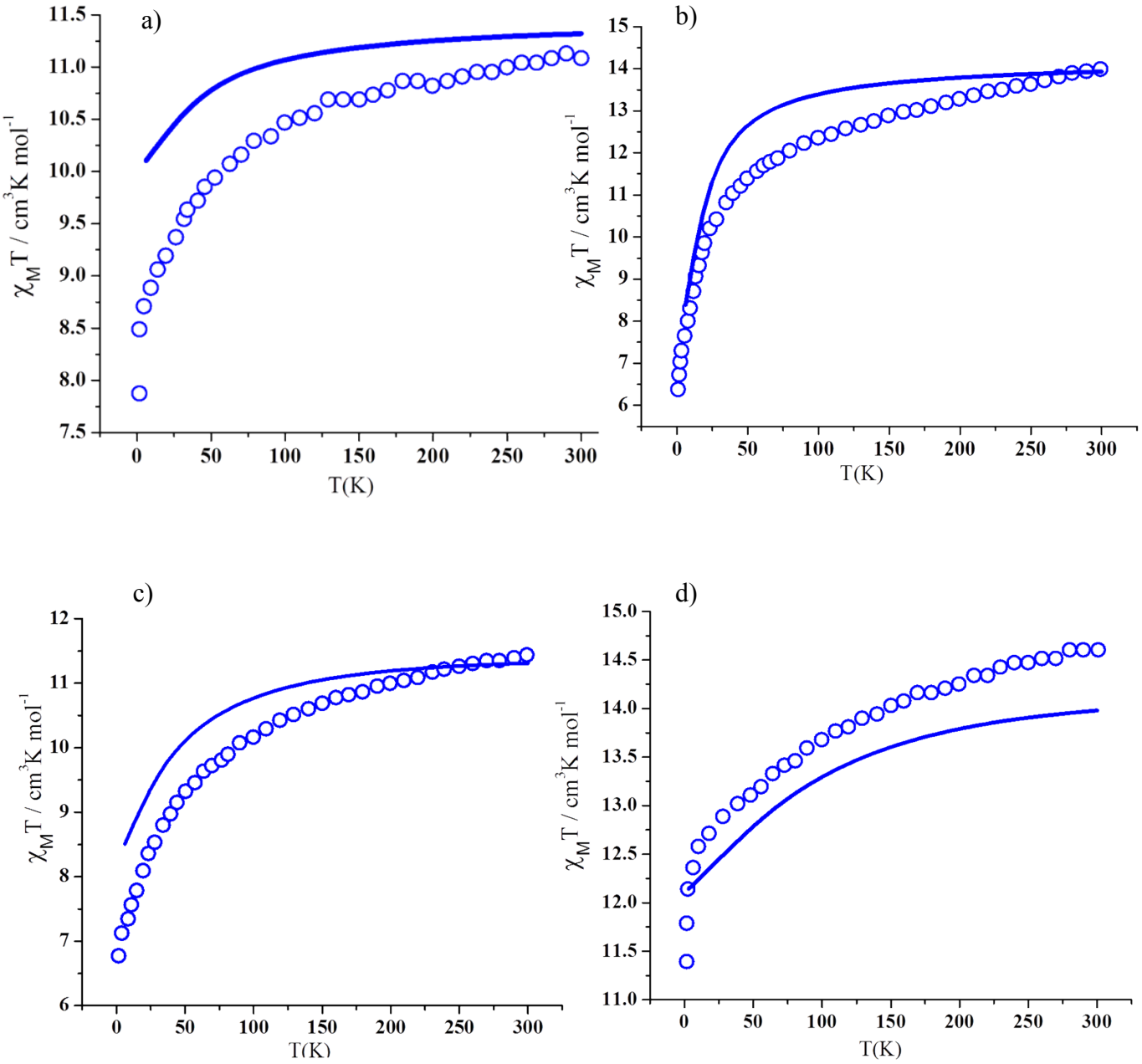

Figure S3. Experimental and *ab initio* computed molar magnetic susceptibility plots for complexes a) **1a**, b) **1b**, c) **2a** and d) **2b**. The blue hollow circles, in all four plots are the experimental magnetic susceptibility extracted from the experimental plots. [14-18] The solid blue lines are the *ab initio* computed molar magnetic susceptibilities. Note the intermolecular interactions zJ is taken as zero in these calculations.

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Out of Plane Shift

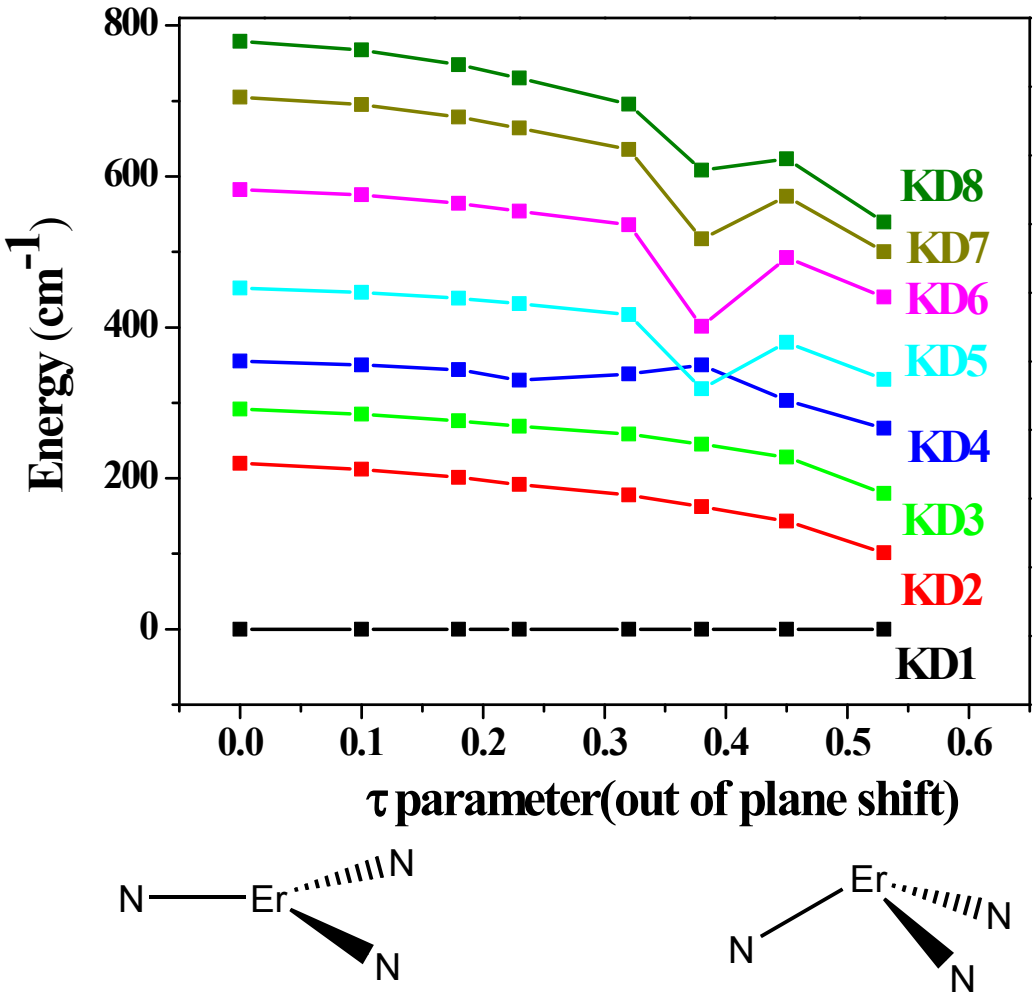

Figure S4. The *ab initio* computed energy levels as a function of out of plane shift parameter (**τ**). All the points have been generated from the CASSCF+RASSI calculations on each structure.

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Table S10. SINGLE_ANISO computed g-tensors and relative energies of eight low lying Kramers doublets as well the orbital magnetic moment $<L_z>$ component associated with each KDs varying out of plane shift parameter (**τ)** in complex **1a**.

KDs Energy(cm^{-1})	g_{xx}	g_{yy}	g_{zz} **τ- 0.0**	θ
0.000	0	0	17.86	0
219.50	0.03	0.03	15.48	0.07
291.82	0.02	0.03	13.05	0.03
355.14	0.01	0.02	10.61	0.16
452.18	1.31	1.34	8.07	0.04
582.39	1.10	1.61	5.70	0.08
704.92	0.11	0.35	3.62	1.27
779.04	9.64	9.38	1.15	0.02

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KDs Energy(cm^{-1})	g_{xx}	g_{yy}	g_{zz}	θ	*KDs Energy(cm^{-1})*	g_{xx}	g_{yy}	g_{zz}	θ
			τ- 0.1					**τ- 0.18**	
0.000	0	0	17.86	0	0.000	0	0	17.86	0
211.73	0.03	0.03	15.48	0.05	200.98	0.04	0.04	15.48	0.05
284.82	0.03	0.03	13.05	0.03	276.29	0.03	0.04	13.03	0.1
349.90	0.02	0.02	10.6	0.01	343.84	0.03	0.03	10.57	0.08
446.43	1.58	1.61	8.01	0.08	438.48	1.93	1.99	7.92	0.16
575.40	1.61	1.65	5.65	0.05	564.09	1.96	2.02	5.57	0.17
695.29	0.19	0.22	3.63	0.59	678.69	0.18	0.22	3.65	1.29
767.78	9.70	9.32	1.15	0.09	747.85	9.70	9.31	1.15	0.17

KDs Energy(cm^{-1})	g_{xx}	g_{yy}	g_{zz}	θ	*KDs Energy(cm^{-1})*	g_{xx}	g_{yy}	g_{zz}	θ
			τ- 0.23					**τ- 0.32**	
0.000	0.0000	0.0000	17.86	0	0.000	0.0000	0.0000	17.86	0
191.73	0.05	0.07\5	15.48	0.09	177.90	0.07	0.07	15.49	0.07
268.82	0.04	0.05	13.02	0.11	258.65	0.06	0.08	12.98	0.19
338.32	0.03	0.04	10.53	0.09	330.14	0.02	0.03	10.44	0.04
431.20	2.26	2.32	7.83	0.20	416.98	3.30	3.35	7.49	0.23
554.11	2.28	2.35	5.49	0.26	535.77	3.29	3.39	5.17	0.57
664.18	0.19	0.24	3.66	1.49	635.42	0.26	0.32	3.70	2.25
730.53	9.70	9.29	1.14	0.21	695.83	9.77	9.19	1.13	0.24

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KDs Energy(cm^{-1})	g_{xx}	g_{yy}	g_{zz}	θ	*KDs Energy(cm^{-1})*	g_{xx}	g_{yy}	g_{zz}	θ
			τ- 0.38					**τ- 0.45**	
0.000	0	0	17.86	0	0.000	0	0	17.87	0
162.37	0.08	0.08	15.49	0.01	143.21	0.1	0.1	15.49	0.12
245.20	0.08	0.09	12.95	0.16	228.09	0.08	0.11	12.91	0.29
349.90	0.03	0.04	10.36	0.07	303.19	0.04	0.08	10.24	0.13
318.66	3.91	3.97	7.21	0.08	380.22	4.63	4.75	6.80	1.35
401.40	3.89	4.00	4.91	1.12	492.40	4.51	4.52	4.86	88.13
516.94	0.25	0.34	3.73	2.49	573.57	0.05	0.24	3.79	2.1
608.38	9.76	9.16	1.12	0.28	623.45	9.55	9.32	1.10	0.25

KDs Energy(cm^{-1})	g_{xx}	g_{yy}	g_{zz}	θ
			τ- 0.53	
0.000	0.00	0.00	17.88	0
101.38	0.13	0.13	15.48	0.074
180.10	0.06	0.19	12.82	0.490
266.35	0.08	0.22	9.92	0.335
331.06	5.75	5.97	6.30	79.57
439.92	6.12	6.03	3.51	1.294
500.34	0.21	0.42	3.97	4.469
779.04	9.64	9.38	1.15	0.705

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Table S11. CASSCF+RASSI computed spin-free energies and spin-orbit state energies for complex **1b**. The SO states energies obtained here by mixing 21 sextets+108 quartets+32 doublets which falls under 40,000 cm^{-1} of energy range.

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Table S12. CASSCF+RASSI computed spin-free energies and spin-orbit state energies for complex **2b**. The SO states energies obtained here by mixing 21 sextets+108 quartets+32 doublets which falls under 40,000 cm^{-1} of energy range.

Spin-free energies for complex 1b Spin-free energies for complex 2b				Spin-Orbit energies for complex 1b Spin-Orbit energies for complex 2b			
0	25763.012	31679.558	39056.318	0	15282.285	29488.002	34987.946
0	25541.812	31427.379	38967.973	0	15153.753	29310.633	34945.352
51.092	25767.68	31683.994	39058.232	48.993	15342.928	29653.833	35172.21
8.836	25569.403	31447.558	39016.53	197.622	15181.794	29321.158	34991.217
34.169	25776.812	31684.153	39138.476	148.96	16172.767	29817.352	35291.758
314.164	25603.364	31447.864	39033.982	372.556	16033.777	29676.344	35079.927
232.769	25778.406	33265.591	39139.21	306.535	16227.757	29972.391	35301.633
329.352	25626.167	33089.13	39056.383	405.172	16056.782	29737.359	35206.2
237.638	25819.698	33267.577	39208.673	520.516	16690.783	30003.926	35328.122
431.132	25636.678	33159.706	39065.403	458.406	16516.342	29780.612	35264.085
339.673	25903.462	33315.57	39291.694	787.184	25108.189	30006.019	35383.718
439.87	25650.218	33225.126	39077.261	519.054	25118.8	29825.003	35296.053
622.881	25938.543	33419.791	39346.924	1071.428	25145.869	30023.986	35390.634
537.952	25660.573	33275.071	39096.991	575.819	25221.547	29843.844	35305.357
1036.959	25939.065	33420.228	39347.389	1329.144	25204.522	30062.894	35430.559
597.409	25761.447	33285.978	39191.504	782.052	25277.395	29879.117	35319.638
1037.306	25979.983	34754.539	39416.066	3584.29	25360.752	30133.561	35490.977
614.603	25762.877	34613.287	39212.006	3624.647	25290.828	29910.634	35353.401
1421.949	25982.087	34778.318	39416.241	3643.11	25399.373	30140.686	35534.086
821.112	25771.471	34618.786	39241.286	3769.66	25362.38	29946.216	35380.445
1422.097	25996.301	34779.913	39468.295	3756.004	25534.001	30164.819	35640.095
821.541	25776.503	34671.493	39249.505	3862.585	25382.627	29973.561	35435.182
7812.109	26407.36	34827.416	39469.7	3921.082	25597.99	30199.533	35664.248
7742.315	26380.297	34689.225	39258.112	3921.252	25439.461	29994.739	35596.103
7861.956	26468.508	34829.503	39506.848	4133.166	25630.523	30227.091	35692.643
7772.404	26394.625	34706.917	39331.385	3965.259	25466.968	30006.579	35627.28
8130.451	26470.45	34871.057	39506.854	4395.146	25688.309	30251.248	35736.206
7832.536	26525.198	34726.684	39336.17	4040.56	25493.325	30035.12	35651.945
8132.188	26676.283	34932.518		4704.087	25725.982	30282.31	35778.266
7882.791	26528.582	34744.9		4179.024	25580.189	30103.479	35674.209
8200.34	26677.947	34965.603		6184.377	25769.969	30310.904	35821.646
7976.274	26611.529	34776.675		6209.204	25627.702	30163.02	35695.511
8201.097	26937.584	34966.555		6243.79	25812.671	31413.886	35865.494
7999.568	26614.136	34786.204		6324.451	25701.292	31267.113	35701.941
8223.899	26981.943	35055.315		6359.819	26013.31	31424.705	35906.71
8039.494	26641.197	34801.649		6406.906	25757.326	31307.908	35712.116
34791.991	27110.101	35055.726		6536.402	27766.467	31458.205	35949.306
34704.092	26697.147	34828.534		6473.111	27729.578	31331.979	35730.899
34794.509	27110.162	37630.28		6785.771	27821.808	31463.296	35976.783
35186.385	26722.503	37673.052		6544.398	27843.569	31400.009	35747.804
36349.872	29838.049	37904.736		7147.887	27939.568	31492.97	35992.415
35485.723	29748.064	37853.678		6642.099	27927.08	31457.288	35801.28
24909.409	29856.398	37905.174		8174.926	28112.922	31576.649	36953.348
24849.315	29750.052	37875.786		8191.901	27975.598	31476.407	36956.165
24937.341	29858.601	38101.825		8241.749	28314.137	31606.007	37099.26
24850.7	29791.359	37930.233		8292.852	28032.944	31519.251	37130.864
24938.342	29894.552	38208.33		8388.185	28464.47	31623.293	37226.879
24971.673	29794.112	37981.494		8384.377	28079.679	31529.76	37204.03
25012.971	29896.138	38271.052		8631.02	28496.869	31918.143	37271.996
24992.33	29867.646	38083.813		8460.475	28552.907	31893.838	37226.656
25014.021	29901.081	38271.63		9022.391	28535.592	31971.053	37333.399
25024.525	29874.747	38112.225		8554.687	28639.977	32019.219	37268.813
25081.929	29940.517	38418.084		9702.458	28634.392	32077.549	37433.048
25073.006	29884.358	38139.809		9743.858	28693.507	32094.869	37335.453
25124.53	29941.629	38419.61		9814.909	28701.359	32235.723	37478.293
25078.033	29894.681	38177.585		9844.96	28738.621	32131.479	37425.655
25174.882	29943.553	38566.397		10091.413	28766.943	32433.143	37506.333
25090.763	29910.792	38202.172		9955.624	28762.543	32185.468	37504.759
25210.896	29993.233	38568.884		10145.589	28813.188	32664.065	37562.856
25096.138	29916.48	38296.967		10085.326	28771.178	32297.872	37570.647
25315.857	29994.089	38631.465		10301.021	28836.968	33047.85	37625.051
25175.772	29933.66	38321.722		10161.026	28800.952	33008.292	37592.692
25316.888	30085.999	37428.397		10401.278	28862.952	33101.425	37699.805
25178.524	29937.819	37312.745		10177.973	28841.257	33026.652	37602.769
25326.87	30089.289	37442.488		10466.38	28912.138	33144.21	37760.704
25218.022	29952.911	37319.376		10216.645	28868.776	33048.66	37633.324
25327.855	30192.097	37443.781		10507.139	28953.422	33184.621	37843.266
25236.577	30001.135	37323.761		10266.344	28887.512	33063.882	37666.622
25409.409	30192.108	37485.522		10519.058	28971.993	33217.524	37926.769
25280.742	30005.791	37330.577		10341.465	28962.45	33075.326	37690.554
25434.882	31491.545	37486.673		10543.122	29048.84	33239.496	38008.332
25287.889	31263.091	37342.625		10362.332	28991.833	33093.272	37722.751
25494.916	31498.411	37531.9		10820.43	29064.268	33260.832	38067.363
25321.298	31265.669	37369.021		10922.259	29014.531	33113.692	37777.377
25496.799	31499.061	37614.473		11240.795	29065.582	33264.45	38878.349
25330.949	31280.332	37385.991		11115.511	29029.66	33153.735	38786.676
25503.503	31517.082	37667.756		11815.39	29132.059	33265.829	38926.708
25353.526	31285.305	37404.201		11328.487	29051.135	33164.755	38880.131
25504.239	31517.402	37670.122		11816.297	29220.596	33760.434	38944.398
25360.554	31287.561	37486.978		11699.569	29076.107	33781.841	38915.916
25550.926	31535.985	37693.588		11868.243	29229.113	33842.388	39037.437
25386.435	31290.619	37504.57		11732.11	29091.669	33859.49	38952.032
25551.197	31568.455	37695.016		11915.358	29255.541	33872.368	39115.77
25411.414	31324.373	37544.002		11770.371	29108.822	33878.338	39046.824
25557.314	31578.954	37705.735		11962.317	29259.4	34119.251	39156.492
25416.698	31340.112	37563.69		11788.376	29141.685	33988.426	39074.632
25596.306	31579.2	37706.49		11988.611	29284.061	34124.233	39202.075
25438.057	31352.119	37587.896		11815.908	29155.684	34012.534	39096.374
25602.815	31585.886	37718.362		13798.78	29311.371	34215.047	39233.075
25450.335	31365.535	37599.144		13630.678	29176.238	34082.474	39113.009
25603.898	31586.295	37725.454		13833.763	29314.175	34302.655	39268.567
25497.506	31370.914	37605.128		13689.322	29194.733	34134.562	39132.879
25609.194	31676.055	37735.886		13843.877	29322.876	34587.79	39302.37
25504.721	31405.602	37628.209		13717.924	29222.792	34216.067	39139.305
25709.306	31677.011	37736.351		13899.604	29330.13	34809.667	………..
25520.006	31407.853	37649.646		13735.854	29264.138	34767.947	………..
25709.839	31677.853	39023.915		13281.274	29348.06	34872.373	

25527.821 31426.514 38964.168	15111.961 29288.896 34878.916

Table S13. SINGLE_ANISO computed g-tensors and relative energies of eight low lying Kramers doublets obtained by calculating 21 sextets+108 quartets+32 doublets for complex **1b**.

KDs Energy(cm^{-1})	g_{xx}	g_{yy}	g_{zz}
0	10.919	10.283	1.371
48.993	0.101	0.529	4.150
148.96	1.200	1.623	6.761
306.535	1.389	1.398	9.458
520.516	0.004	0.006	12.159
787.184	0.006	0.008	14.678
1071.428	0.008	0.009	17.218
1329.144	0.000	0.000	19.792

Table S13. SINGLE_ANISO computed g-tensors and relative energies of eight low lying Kramers doublets obtained by calculating 21 sextets+108 quartets+32 doublets for complex **2b**.

KDs Energy(cm^{-1})	g_{xx}	g_{yy}	g_{zz}
0	0.007	0.012	19.591
197.622	0.059	0.068	17.089
372.556	0.272	0.425	14.659
405.172	0.736	0.951	19.014
458.406	0.575	6.651	8.900
519.054	0.940	1.319	13.360
575.819	0.425	0.841	16.785
782.052	0.004	0.006	19.798

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