Supplementary Material

Control of the geometry and anisotropy driven by the combination of steric and anion coordination effects in Co^{II} complexes with N_6-tripodal ligands: The impact of the size of the ligand on the magnetization relaxation time.

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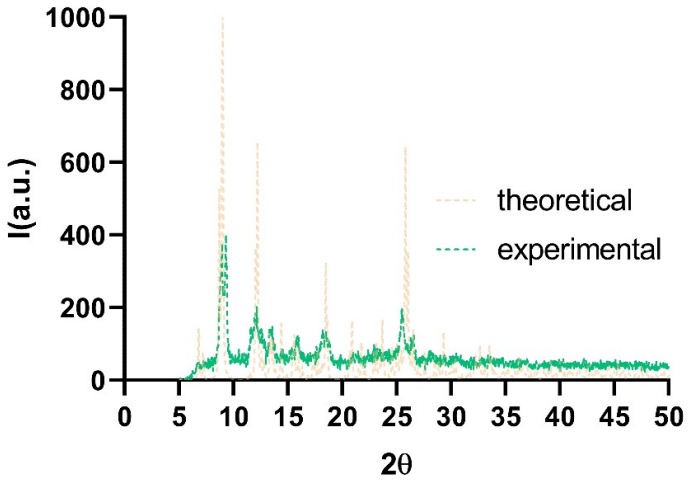
Table S1. Crystallographic data and structural refinement details for complexes **1-4.**

Compound	**1**	**2**	**3**	**4**
Formula	$C_{36.25}H_{39}CoN_{11}O_{3.25}PS_3$	$C_{37}H_{38}Cl_2CoN_{11}OPS$	$C_{36}H_{37}CoN_{11}O_{2.5}PS_3$	$C_{35}H_{38}Cl_2CoN_9O_{10}PS$
M_r	866.67	845.64	849.84	937,60
Crystal System	triclinic	monoclinic	monoclinic	monoclinic
Space Group	P-1	C2/c	C2/c	$P2_1/n$
a (Å)	7.556(6)	27.738(3)	27.919(3)	15.799(7)
b (Å)	16.398(14)	13.8757(12)	13.999(13)	15.173(6)
c (Å)	18.651(15)	21.707(2)	20.960(2)	17.531(7)
α (º)	77.604(2)	90	90	90
β (º)	79.837(2)	110.717(3)	107.188(3)	104.778(10)
γ (º)	85.377(2)	90	90	90
V (Å^3)	2219.3(3)	7814.4(13)	7826.2(14)	4063.6(3)
Z	2	8	8	4
Dc (g cm^{-1})	1.297	1.438	1.443	1.533
μ(MoK$_α$) (mm^{-1})	0.611	0.717	0.690	0.712
T (K)	100(2)	100(2)	100(2)	100(2)

Observed reflections[a]	4664 (3804)	9754 (8676)	9704 (8230)	10054 (7234)
$\mathbf{R_{int}}^{a}$	0.0513 (0.0407)	0.0361 (0.0349)	0.0417 (0.0368)	0.0562 (0.0489)
Parameters	489	495	606	544
GOF	1.066	1.235	1.078	1.081
$\mathbf{R_1}^{b,a}$	0.0932 (0.0754)	0.0574 (0.0500)	0.0627 (0.0511)	0.1167 (0.0824)
$\mathbf{wR_2}^{c,a}$	0.2259 (0.2105)	0.1198 (0.1228)	0.1296 (0.1235)	0.2252 (0.2010)
[a] Values in parentheses for reflections with I > 2s(I) [b] $R1 = \sum\|\|Fo\| - \|Fc\|\|/\sum\|Fo\|$ [c] $wR2 = \{\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]\}^{½}$				

Powder DRX and ESI mass spectrometry

To confirm the homogeneity and purity of the crystalline products, X-ray powder diffractograms have been made for compounds **1-4** and **4'**. However, the diffraction of **1** and **4** is very poor and absent in the case of **4'**, so only the powder diffractograms of **2** and **3** have been compared with the theoretical one obtained from the crystalline structures determined by single crystal X-ray diffraction (Figure S1). In both cases, the experimental and theoretical spectrum are practically coincident which indicate that the samples are pure.



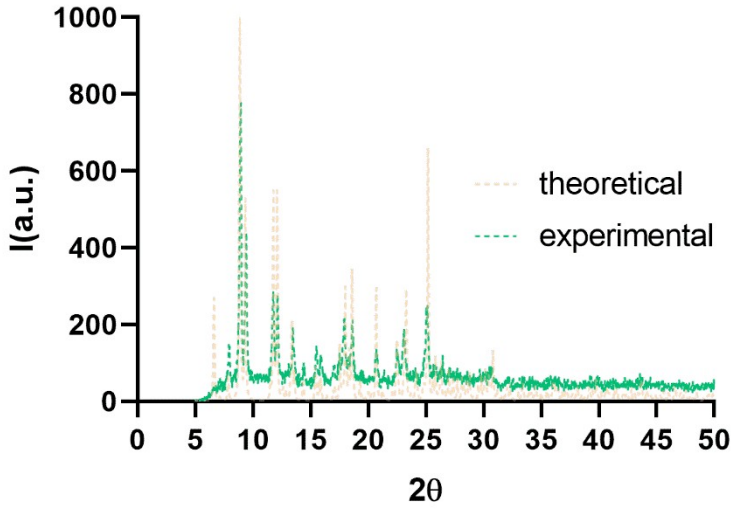


Figure S1. Experimental (green) and theoretical (orange) X-ray powder diffractograms of complexes **2** (top) and **3** (bottom)

For compounds **1**, **4** and **4'**, mass spectrum (ESI-MS) has been recorded to confirm that the molecular ion is observed and therefore the compound is found in the sample (see experimental part). Moreover, the experimental elemental analysis verifies that the solid sample composition match well with the theoretical complexes' composition (see experimental part). Then, the elemental analysis, together with the mass spectrum, indicates that the samples are pure.

Table S2. Selected bond distances and angles for complex **1**

Selected bond distances (Å)			
Co1-N4	2.155 (6)	Co1-N7	2.165 (6)
Co1-N10	2.038 (8)	Co1-N11	2.059 (8)
Co1-S1	2.574 (2)	Co1-O1	2.105 (6)
Selected bond angles (°)			
N4-Co-N7	76.4 (2)	N4-Co-N10	97.1 (3)
N4-Co-S1	84.15 (18)	N4-Co-O1	84.0 (2)
N7-Co1-N10	89.7 (3)	N7-Co1-O1	87.1 (2)
N10-Co1-S1	92.3 (19)	S1-Co1-O1	91.27 (17)
N11-Co1-N7	110.8 (3)	N11-Co1-N10	92.4 (3)
N11-Co1-S1	88.4 (2)	N11-Co1-O1	87.0 (3)
N4-Co1-N11	168.1 (3)	N7-Co1-S1	160.57 (16)
N10-Co1-O1	176.4 (3)		

Table S3. Selected bond distances and angles for **2** and **3**

Selected bond distances (Å)							
2				**3**			
Co1-N4	2.169	Co1-N5	2.175	Co1-N4	2.163	Co1-N5	2.151
Co1-N7	2.145	Co1-N8	2.130	Co1-N7	2.134	Co1-N8	2.137
Co1-Cl1	2.411	Co1-Cl2	2.447	Co1-N10	2.097	Co1-N11	2.048
Selected bond angles (°)							
2				**3**			
N4-Co1-N5	93.01	N4-Co1-N7	75.89	N4-Co1-N5	93.51	N4-Co1-N7	76.10
N5-Co1-N8	76.03	N7-Co1-N8	114.49	N5-Co1-N8	76.91	N7-Co1-N8	112.74
Cl1-Co1-N4	101.15	Cl1-Co1-N5	99.54	N10-Co1-N4	83.57	N10-Co1-N5	88.30
Cl1-Co1-N7	87.45	Cl1-Co1-N8	86.32	N10-Co1-N7	86.32	N10-Co1-N8	88.38
Cl2-Co1-N4	88.82	Cl2-Co1-N5	85.29	N11-Co1-N4	100.06	N11-Co1-N5	100.71
Cl2-Co1-N7	89.68	Cl2-Co1-N8	86.32	N11-Co1-N7	85.52	N11-Co1-N8	89.43
N4-Co1-N8	167.72	N5-Co1-N7	167.92	N4-Co1-N8	167.70	N5-Co1-N7	168.77
Cl1-Co1-Cl2	168.60			N10-Co1-N11	169.99		

Table S4. Selected bond distances and angles for compound **4**.

Selected bond distances (Å)			
Co1-N4	2.126 (4)	Co1-N7	2.138 (4)
Co1-N5	2.122 (4)	Co1-N8	2.139 (4)
Co1-N6	2.102 (4)	Co1-N9	2.115 (4)
Selected bond angles (°)			
N4-Co1-N5	83.78 (15)	N4-Co1-N6	85.35 (16)
N4-Co1-N7	74.52 (15)	N4-Co1-N8	110.49 (15)
N5-Co1-N6	86.15 (16)	N5-Co1-N8	75.45 (16)
N5-Co1-N9	114.51 (16)	N6-Co1-N7	110.52 (16)
N6-Co1-N9	76.06 (17)	N7-Co1-N8	94.17 (15)
N7-Co1-N9	92.97 (16)	N8-Co1-N9	94.57 (17)
N4-Co1-N9	152.45 (18)	N5-Co1-N7	151.01 (16)
N6-Co1-N8	153.79 (17)		

Table S5. Obtained S values with the SHAPE software and τ_6 values for the (OC-6) and (TPR-6) geometries for complexes **1-4**.

Complex	S(OC-6)	S(TPR-6)	τ6
1	1.694	11.454	0.23
2	2.327	11.832	0.24
3	1.824	11.617	0.22
4	5.602	4.322	0.55

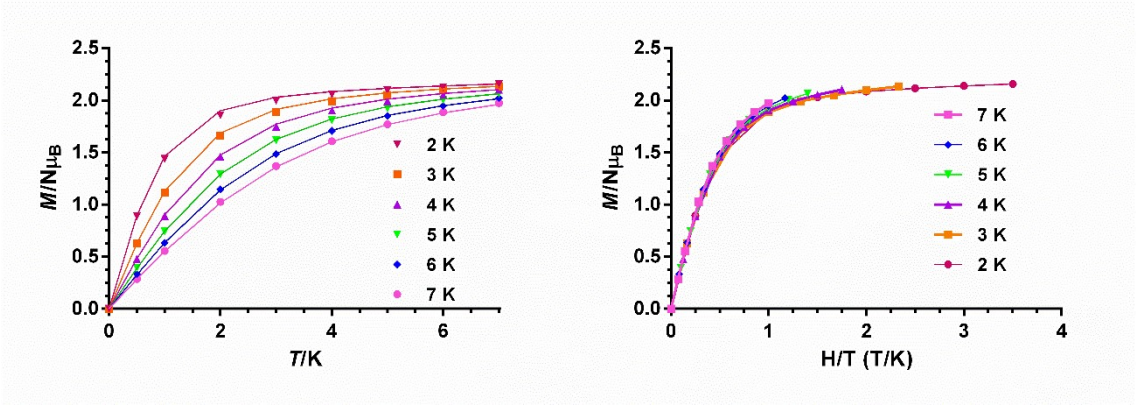


Figure S2.- Temperature dependence of Mvs H and M vs H/T plots for **1**. Solid lines represent the best fit to equation 1.

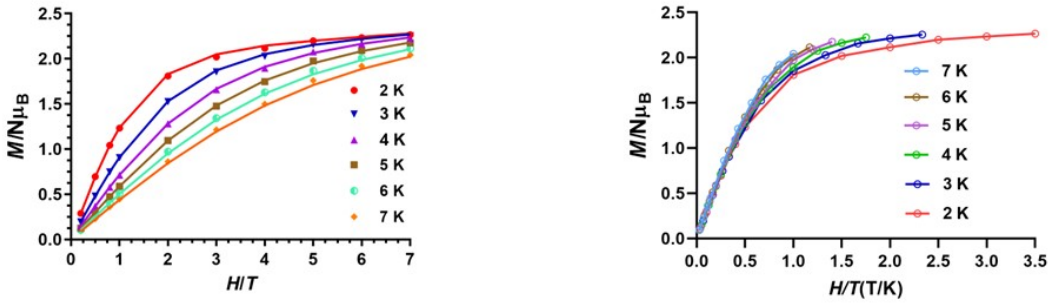


Figure S3.- Temperature dependence of Mvs H and M vs H/T plots for **2**. Solid lines represent the best fit to equation 1.

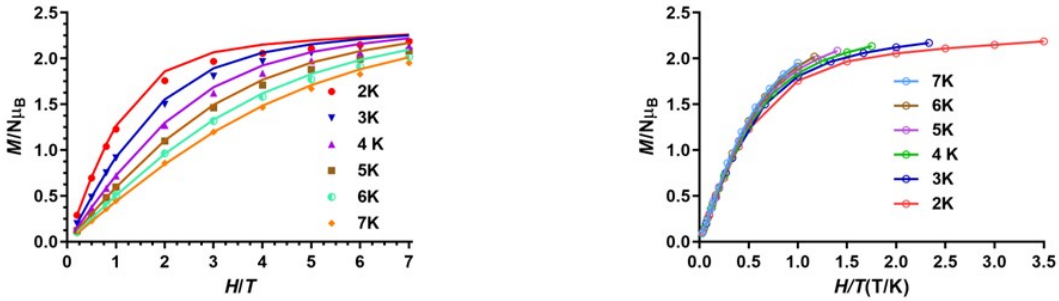


Figure S4.- Temperature dependence of Mvs H and M vs H/T plots for **3**. Solid lines represent the best fit to equation 1.

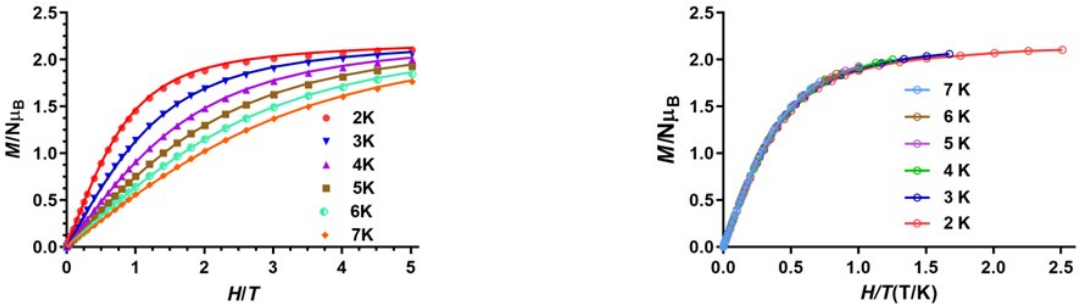


Figure S5.- Temperature dependence of Mvs H and M vs H/T plots for **4**. Solid lines represent the best fit to equation 1.

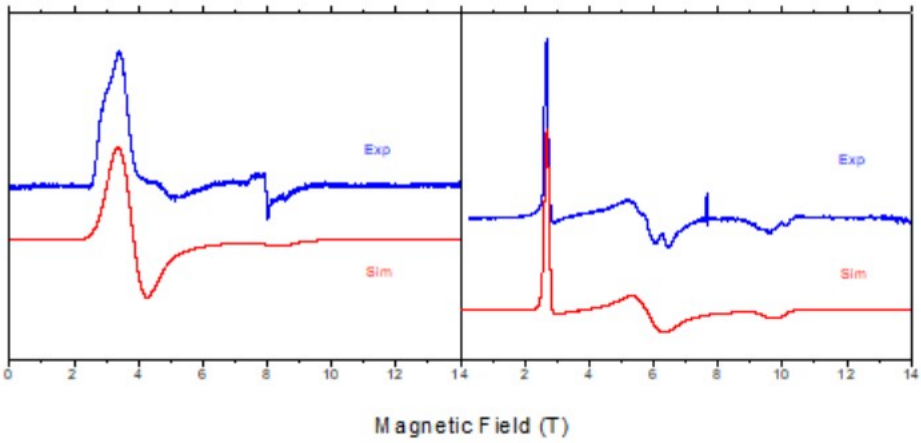


Figure S6.- HFEPR spectra of **2** (left) and **3** (right) as a pellet recorded at 10 K and 119 GHz (blue trace) and their simulation (red trace) using the D and E values indicated on Table 1.

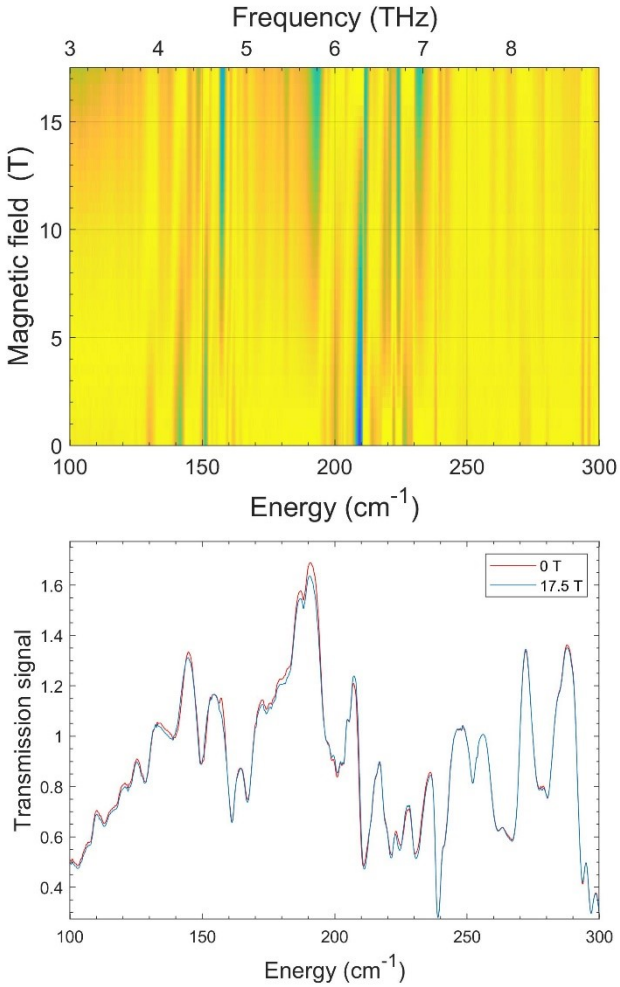


Figure S7.- (Top) Experimental (magnetic field vs. energy) heatmaps of FIRMS response for complex **4**. Blue and yellow regions represent resonance absorptions sensitive and insensitive to the field, respectively. (Bottom) Far-infrared transmission spectra measured at two magnetic fields.

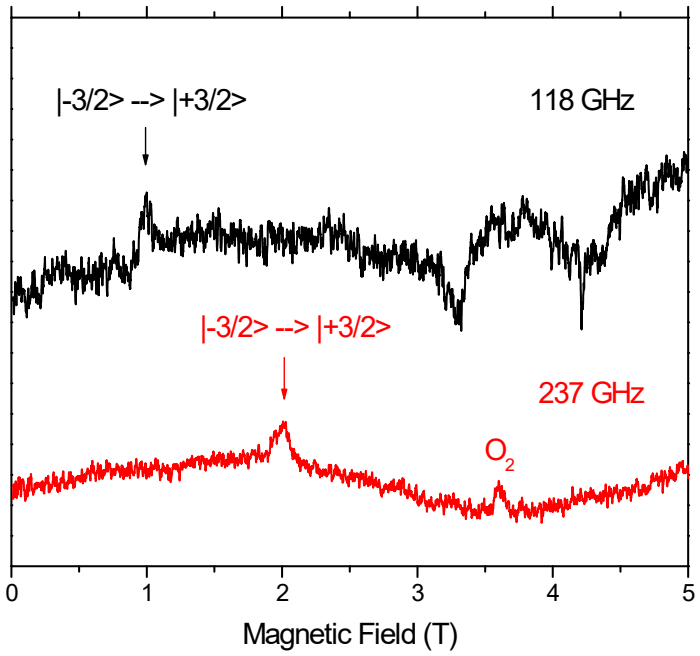


Figure S8.- HFEPR spectra of **4** as a pellet recorded at 10 K and 118 GHz (black trace) and 237 GHz (red trace).

Table S6.- The xyz coordinates for the computed structures are gathered below.

Compound **1**			
Co	0.00000	0.00000	0.00000
S	2.57408	-0.00000	0.00000
P	2.71358	-1.93322	0.03591
S	-0.41067	-0.11039	4.77503
O	-0.04724	0.30429	-2.08040
N	1.44298	-2.68140	-0.75405
N	2.78323	-2.54670	1.56807
N	0.21908	-2.07534	-0.53770
N	2.80643	-3.91761	1.59002
N	4.02507	-2.55712	-0.80307
N	5.12240	-2.68726	0.03025
N	-0.08124	-0.27085	2.01895
N	0.05804	2.04953	0.18928
C	-0.22058	-0.22000	3.17410
C	-0.87577	-2.67359	-0.82201
H	-0.87507	-3.55418	-1.17920
C	3.17925	-4.51788	2.65163
H	3.56616	-4.06695	3.39226
C	1.45476	-4.04881	-1.25149
H	2.37832	-4.36847	-1.30854
H	1.04336	-4.07548	-2.14112
H	0.94655	-4.62225	-0.64028
C	4.17566	-2.23796	-2.20939
H	3.29224	-2.11023	-2.61303
H	4.63942	-2.97276	-2.66306
H	4.69980	-1.41470	-2.30274
C	3.17930	-1.77177	2.74104
H	4.10751	-1.98301	2.97379
H	2.59437	-1.99747	3.49447
H	3.10156	-0.81562	2.54213
C	6.30153	-2.73367	-0.47469
H	6.37311	-2.68069	-1.42058
N	-2.04161	-0.69961	-0.16554
C	-2.12690	-1.95517	-0.58013
C	-3.33942	-2.62961	-0.77225
H	-3.34557	-3.53259	-1.06819
C	-4.50560	-1.97599	-0.53010
H	-5.33681	-2.41303	-0.67229
C	-4.47529	-0.65247	-0.06660
C	-5.64826	0.08921	0.24107
H	-6.50255	-0.30942	0.12718
C	-5.55449	1.35464	0.69377
H	-6.34449	1.83730	0.90554
C	-4.30693	1.96397	0.85530
H	-4.26045	2.86419	1.15537
C	-3.15256	1.27706	0.58506
H	-2.31134	1.69209	0.72976
C	-3.21068	-0.02915	0.09893
N	8.66902	-2.71845	-0.37189
C	7.53175	-2.85986	0.27645
C	7.35994	-3.13961	1.62938
H	6.49533	-3.22972	2.01276
C	8.49228	-3.28407	2.37571
H	8.42913	-3.47189	3.30515
C	9.75190	-3.15724	1.76899
C	10.95199	-3.28904	2.52258
H	10.91316	-3.45116	3.45755

Compound **2**			
Co	0.00000	0.00000	0.00000
Cl	-0.20011	0.43995	-2.39853
P	2.38912	-2.61253	-0.24982
Cl	0.00000	-0.00000	2.41108
S	3.66009	-3.97027	-0.73606
N	0.54076	2.05595	0.13664
N	2.14458	0.00382	-0.36072
N	2.90343	-1.08712	-0.75613
N	-2.11021	-0.37283	0.09537
C	0.03457	4.41335	0.20393
H	-0.61031	5.10182	0.32115
N	2.09992	-2.34764	1.37659
N	-0.18191	-2.12021	-0.41924
N	0.85694	-2.91579	-0.86491
C	3.66159	3.98526	-0.56930
H	4.31048	3.29298	-0.62340
C	0.53614	-4.12321	-1.62542
H	1.36050	-4.51062	-1.98617
H	-0.06789	-3.89287	-2.36227
H	0.10053	-4.77302	-1.03567
N	1.32510	-3.35520	1.93304
C	-3.82681	-2.09565	-0.03143
C	-0.31345	3.08665	0.37182
H	-1.19350	2.88464	0.66673
C	-4.23303	-3.43053	-0.26088
H	-3.59436	-4.07934	-0.53021
C	-0.26136	-5.51576	3.40607
C	2.66060	1.18222	-0.47074
H	3.56596	1.29881	-0.73555
C	-6.16201	-1.54745	0.52079
H	-6.82143	-0.91409	0.78192
C	1.80422	2.33116	-0.17214
N	0.92606	-4.47414	5.24858
C	-2.47833	-1.63450	-0.14917
C	-4.39949	0.19458	0.57534
H	-5.03798	0.85950	0.80685
C	0.64453	-4.55257	3.95018
C	-0.86247	-6.42750	4.32305
C	-3.07081	0.52211	0.44797
H	-2.81021	1.41942	0.61568
C	-1.39567	-2.53650	-0.54295
H	-1.58281	-3.40489	-0.88130
C	2.30901	3.66503	-0.28896
C	3.08767	6.32998	-0.68411
H	3.35653	7.22683	-0.84877
C	-0.53800	-6.32544	5.69052
H	-0.92867	-6.91811	6.32187
C	1.40231	-3.53092	3.19765
H	1.98727	-2.96590	3.68657
C	4.03390	5.29032	-0.76293
H	4.94147	5.49642	-0.95398
C	-4.81055	-1.13946	0.35865
C	1.36473	4.72451	-0.14543
C	-1.47196	-6.57254	1.59978
H	-1.68866	-6.62509	0.67704
C	-5.55047	-3.79539	-0.09630
H	-5.80806	-4.69618	-0.25394

C	12.14396	-3.18042	1.90341
H	12.94467	-3.27796	2.40427
C	12.21017	-2.91839	0.52310
H	13.05810	-2.84303	0.10003
C	11.06252	-2.77730	-0.23178
H	11.12250	-2.61167	-1.16413
C	9.80866	-2.87043	0.39101
N	3.78095	-6.67234	3.43975
C	2.94914	-6.01808	2.62384
C	1.96996	-6.69739	1.87259
H	1.37247	-6.20336	1.32353
C	1.87040	-8.05887	1.92148
H	1.18929	-8.50715	1.43952
C	2.78767	-8.77848	2.69849
C	2.78225	-10.20331	2.80239
H	2.16489	-10.70879	2.28319
C	3.63475	-10.84017	3.61819
H	3.61907	-11.79124	3.65424
C	4.54360	-10.13843	4.41749
H	5.12186	-10.60259	5.01212
C	4.58671	-8.76088	4.32235
H	5.21648	-8.28302	4.84738
C	3.72751	-8.05103	3.47219
C	-0.29206	3.15508	0.21528
S	-0.72127	4.72624	0.20868
C	0.51269	1.19101	-2.81626
C	0.34268	-5.36848	6.09423
H	0.56272	-5.32164	7.01731
C	1.78772	6.06175	-0.37428
H	1.16077	6.77358	-0.31137
C	3.09890	-1.64856	2.19489
H	3.71617	-2.30158	2.58588
H	2.64704	-1.15631	2.91118
H	3.59921	-1.02077	1.63234
C	-0.59633	-5.61305	2.03490
H	-0.21206	-5.00946	1.41119
C	4.20977	-0.84965	-1.36156
H	4.80715	-0.44253	-0.70029
H	4.10936	-0.24649	-2.12858
H	4.58827	-1.70125	-1.66388
C	-2.05723	-7.48724	2.50973
H	-2.65421	-8.15358	2.19244
C	-6.52036	-2.85686	0.30183
H	-7.42177	-3.12704	0.41880
C	-1.76532	-7.41484	3.83363
H	-2.16804	-8.02780	4.43878
N	4.87584	1.58469	2.18827
C	2.69026	2.41695	3.28735
H	2.75839	2.34117	4.26183
H	1.94363	1.86743	2.96835
H	2.53438	3.35332	3.04401
C	3.92157	1.95817	2.67872
C	1.98528	-1.87855	-4.61566
N	1.57065	-2.90919	-4.71393
C	2.52984	-0.52529	-4.55008
H	2.21052	-0.08247	-3.73636
H	2.23697	-0.01829	-5.33683
H	3.50764	-0.56877	-4.53508
O	-1.01348	2.70972	3.92409
H	-0.89569	1.88059	3.68600
H	-0.68817	3.23564	3.30968

Compound **3**

Co	0.00000	0.00000	0.00000
P	-1.88941	-2.94977	-0.37120
S	-2.93309	-4.55556	-0.23752
S	0.52668	-1.18828	4.55448
S	1.82592	1.22598	-4.08490
N	2.12930	0.00342	0.13640
N	0.50924	-2.08832	0.24154
N	0.00000	-0.00000	2.09769
N	-2.11682	-0.37216	0.06376
N	0.28951	0.20633	-2.01768
C	4.30130	1.00418	0.10487
H	4.83418	1.78083	-0.01887
C	0.22681	-0.49881	3.11000
C	-2.82741	0.68979	0.23600
H	-3.75653	0.63015	0.42461
N	-2.70737	-1.60758	0.22878
N	-0.40634	-3.09902	0.41690
N	-1.41372	-2.44452	-1.89258
N	-2.51041	-2.01320	-2.63202
C	-4.06880	-1.67314	0.74523
H	-4.69111	-1.33067	0.07019
H	-4.13648	-1.12937	1.55779
H	-4.29400	-2.60353	0.95514
C	6.03625	-2.69225	1.06127

Compound **4**

Co	0.00000	0.00000	0.00000
P	0.00000	0.00000	3.29910
S	-0.00273	-0.02579	5.20364
N	1.65506	0.17446	1.32514
N	-0.23530	1.79120	-1.14450
N	1.69654	-0.67500	-1.11397
N	-0.91901	1.37024	1.33570
N	-1.15639	1.03119	2.63090
N	1.47259	0.50508	2.64158
N	-0.66848	-1.50439	1.30679
N	-0.28336	-1.52090	2.62114
N	-1.35536	-1.12700	-1.17098
C	-1.06746	2.66312	-0.59351
C	2.86200	-0.24408	-0.61520
C	-1.54217	3.82452	-1.30134
C	4.07502	-0.32762	-1.34042
C	4.03339	-0.93602	-2.63397
C	-1.48139	2.38561	0.78601
H	-2.12125	2.91986	1.24129
C	-1.10068	3.99161	-2.64255
C	2.80653	0.26466	0.75677
H	3.56421	0.63485	1.19474
C	-0.17202	3.06300	-3.16636
H	0.16052	3.17320	-4.04906

H	6.43206	-3.53362	1.25584	C	5.30876	0.18340	-0.86572
C	4.90366	-0.21287	0.45900	H	5.35684	0.56607	0.00181
C	4.67657	-2.61032	0.88607	C	0.24509	2.01375	-2.40796
H	4.13872	-3.38971	0.96231	H	0.88927	1.41543	-2.76718
C	6.85188	-1.55284	0.95752	C	2.80358	-1.45780	-3.07954
H	7.78897	-1.62774	1.09425	H	2.75542	-1.92673	-3.90435
C	2.67651	-1.17608	0.42809	C	1.68533	-1.28998	-2.32639
C	-2.40975	-1.97493	-3.91158	H	0.85880	-1.61728	-2.66249
H	-1.59207	-2.18023	-4.34838	C	-2.43686	4.76132	-0.75548
C	4.07829	-1.36102	0.59175	H	-2.70755	4.68358	0.15195
C	1.73830	-2.29029	0.57022	C	-1.61724	5.06194	-3.42309
H	2.02649	-3.13531	0.89465	H	-1.33051	5.18463	-4.32009
C	6.30357	-0.33991	0.66154	C	-1.71781	-2.27496	-0.62530
H	6.86180	0.42545	0.59043	C	-2.21400	1.69842	3.39958
C	0.02315	-4.29798	1.14364	H	-2.31496	1.25698	4.26836
H	-0.75447	-4.86500	1.32699	H	-3.05900	1.64557	2.90582
H	0.44233	-4.03440	1.98945	H	-1.97398	2.63865	3.53637
H	0.66951	-4.79529	0.60002	C	-1.78347	-0.79728	-2.41894
C	0.92756	0.62057	-2.87463	H	-1.55272	0.05314	-2.77355
C	-0.29180	-3.11083	-2.57092	C	6.42376	0.12992	-1.64440
C	2.94811	1.06890	-0.06119	H	7.24540	0.48371	-1.32396
H	2.56213	1.89555	-0.32656	C	5.21398	-0.98400	-3.40242
N	-0.83547	1.96566	0.06051	H	5.20267	-1.39481	-4.25910
C	-2.16264	1.99082	0.13263	C	2.50842	1.22181	3.35977
C	-2.91755	3.20165	0.10692	H	2.18214	1.46007	4.25275
C	-4.33430	3.24800	0.16011	H	2.74256	2.03660	2.86906
H	-4.83151	2.44209	0.23646	H	3.30124	0.65140	3.44361
C	-4.98909	4.45127	0.10139	C	-2.91914	-4.46206	-0.80121
H	-5.93793	4.47167	0.14454	H	-2.67681	-4.69049	0.08856
C	-4.27347	5.65757	-0.02201	C	-2.53424	-3.23165	-1.34113
H	-4.74120	6.48289	-0.06970	C	-2.92243	5.78846	-1.52710
C	-2.90975	5.64710	-0.07344	H	-3.52622	6.41907	-1.15351
H	-2.43335	6.46469	-0.15755	C	6.35687	-0.45737	-2.93612
C	-2.20105	4.42214	-0.00173	H	7.13475	-0.47477	-3.48006
C	-0.79444	4.35855	-0.05206	C	-1.27690	-2.50365	0.74867
H	-0.28442	5.15792	-0.10906	H	-1.42589	-3.32575	1.20159
C	-0.16448	3.14836	-0.01904	C	-2.52578	5.90873	-2.86859
H	0.78469	3.12993	-0.05300	H	-2.90064	6.59841	-3.40270
N	-3.40478	-1.19645	-6.00732	C	-3.68270	-3.80543	-3.43878
C	-3.76771	-1.55261	-4.77446	H	-3.95604	-3.58575	-4.32223
C	-5.12463	-1.53405	-4.37449	C	-2.91498	-2.87454	-2.66723
C	-5.57015	-1.93213	-3.09502	C	-4.01518	-5.00698	-2.89631
H	-4.94177	-2.20161	-2.43474	H	-4.50228	-5.63373	-3.41947
C	-6.89242	-1.92671	-2.80559	C	-2.53684	-1.64959	-3.18257
H	-7.19395	-2.26370	-1.97033	H	-2.79979	-1.39942	-4.06105
C	-7.82931	-1.42559	-3.74264	C	-3.65596	-5.34482	-1.57372
H	-8.74750	-1.37136	-3.50688	H	-3.92142	-6.18234	-1.21176
C	-7.42931	-1.02647	-4.96650	C	-0.38983	-2.75209	3.38176
H	-8.06856	-0.69335	-5.58433	H	-0.07014	-2.59912	4.29498
C	-6.06647	-1.10059	-5.34156	H	0.15615	-3.44607	2.95610
C	-5.65995	-0.73728	-6.63463	H	-1.32526	-3.04060	3.40567
H	-6.28319	-0.43111	-7.28385	Cl	3.99029	-2.57738	2.98914
C	-4.34808	-0.84329	-6.91614	O	4.58533	-1.26374	2.85330
H	-4.06532	-0.65736	-7.80308	O	3.52246	-2.69977	4.24475
H	-0.59986	-3.80529	-3.18880	O	5.18220	-3.40519	2.83812
H	0.34064	-3.52847	-1.83479	O	3.07502	-2.73105	1.91566
H	0.05929	-2.54319	-3.06004	O	2.87927	-6.03353	0.17326
O	0.23132	2.00978	-8.51682	H	3.61358	-5.68190	0.37983
H	-0.16413	1.41795	-8.01594	C	1.85419	-4.97490	0.00542
H	-0.37959	2.35899	-9.02903	H	2.12422	-4.37127	-0.71828

O	3.15695	4.31095	0.59595	H	1.76961	-4.46812	0.83925
H	3.99426	4.27742	0.52909	H	0.99350	-5.38664	-0.21671
C	2.72184	5.57481	0.28335	O	-4.79675	3.47071	1.52364
H	2.29025	5.56199	-0.59591	H	-5.14832	3.18374	2.22990
H	3.48710	6.18637	0.26362	C	-5.55565	3.01600	0.39145
H	2.08024	5.87416	0.95957	H	-5.34802	3.57461	-0.38693
O	-0.81453	-0.03754	-7.07361	H	-6.51264	3.07994	0.59290
H	-0.78127	0.85521	-6.72220	H	-5.32447	2.08423	0.19556
H	-1.64515	-0.42238	-6.78451	O	-5.44461	-1.25815	0.59273
				O	-5.07245	0.00837	2.54617
				Cl	-4.45324	-0.82147	1.55359
				O	-3.45196	-0.06956	0.85922
				O	-3.87113	-1.99040	2.14682

Table S7. Spin Free CASSCF and CASSCF/NEVPT2 energies (δE, cm^{-1}).

States	**1**		**2**		**3**		**4**	
	CASSCF	**NEVPT2**	**CASSCF**	**NEVPT2**	**CASSCF**	**NEVPT2**	**CASSCF**	**NEVPT2**
1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
2	446.0	615.3	1263.0	1658.0	1104.3	1471.9	158.6	217.2
3	709.4	840.8	1588.7	2190.7	1670.9	2286.2	3211.3	4087.6
4	5561.5	7401.4	6104.1	8554.3	8031.3	10730.8	7156.9	9584.5
5	6677.8	8466.3	7421.1	10007.7	8350.5	10998.7	7546.3	10152.7
6	6881.7	8867.4	7578.4	10132.1	8354.7	11015.5	8146.2	10926.4

Table S8. Energy levels after the inclusion of spin-orbit effects from CASSCF and CASSCF/NEVPT2 calculations (ΔE, cm^{-1}).

States	**1**		**2**		**3**		**4**	
	CASSCF	**NEVPT2**	**CASSCF**	**NEVPT2**	**CASSCF**	**NEVPT2**	**CASSCF**	**NEVPT2**
1	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
2	200.70	176.49	86.64	66.59	112.15	88.03	248.91	243.86
3	647.11	755.62	1273.29	1669.05	1199.02	1546.71	584.96	610.54
4	999.98	1082.51	1468.09	1807.35	1376.22	1667.95	909.14	917.90
5	1164.86	1245.12	1846.04	2380.42	1921.48	2471.31	3538.06	4384.92
6	1278.47	1368.85	1931.36	2448.15	1972.35	2516.85	3625.34	4467.24
7	5928.76	7705.95	6284.45	8675.77	8227.05	8492.26	7517.44	9906.17
8	6011.66	7774.37	6356.15	8731.82	8267.49	10857.03	7591.02	9963.13

Table S9. The ligand field one electron eigenfunctions from CASSCF/NEVPT2 calculations.

1

Orbital	Energy (eV)	Energy (cm^{-1})	d_{z^2}	d_{xz}	d_{yz}	$d_{x^2-y^2}$	d_{xy}
1	0.000	0.0	-0.100613	0.666269	-0.205192	0.079458	-0.705368
2	0.014	113.7	-0.130985	-0.736546	-0.084959	0.185577	-0.631416
3	0.081	656.5	-0.233345	-0.078030	-0.926972	-0.192648	0.207535
4	0.817	6593.1	-0.538343	0.086571	0.016264	0.801760	0.244147
5	1.100	8875.2	-0.792752	0.001317	0.301888	-0.528502	-0.033033

2

Orbital	Energy (eV)	Energy (cm^{-1})	d_{z^2}	d_{xz}	d_{yz}	$d_{x^2-y^2}$	d_{xy}
1	0.000	0.0	-0.150138	-0.111570	0.120072	-0.082854	-0.971457
2	0.152	1228.9	0.127338	-0.973986	0.122304	-0.084112	0.114471
3	0.161	1296.3	-0.167668	-0.137725	-0.962847	-0.147160	-0.064727
4	1.069	8620.9	-0.693789	-0.139889	0.028927	0.702689	0.066935
5	1.095	8830.1	0.672152	-0.019149	-0.206673	0.686027	-0.185736

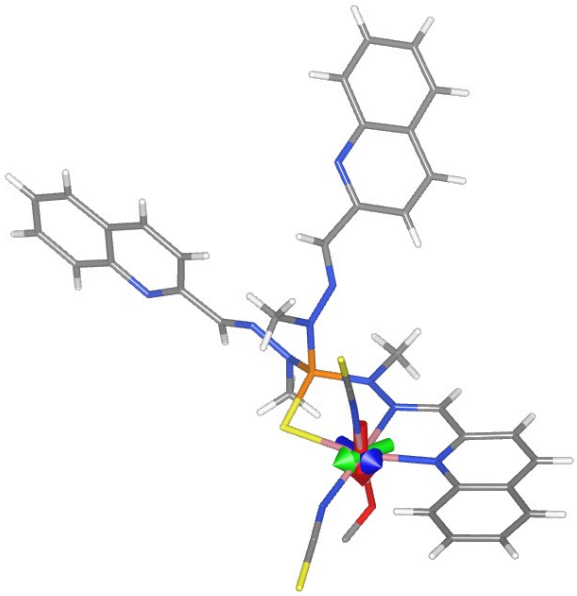
3

Orbital	Energy (eV)	Energy (cm^{-1})	d_{z^2}	d_{xz}	d_{yz}	$d_{x^2-y^2}$	d_{xy}
1	0.000	0.0	-0.129839	-0.036601	0.059702	-0.390087	0.908884
2	0.191	1537.8	-0.000126	-0.419148	0.905202	0.027845	-0.064407
3	0.195	1573.5	-0.095468	-0.901740	-0.419164	0.045205	-0.003016
4	1.113	8974.0	0.043509	0.032758	0.015435	0.915085	0.399269
5	1.414	11405.2	-0.985969	0.093632	0.033289	0.087370	-0.101769

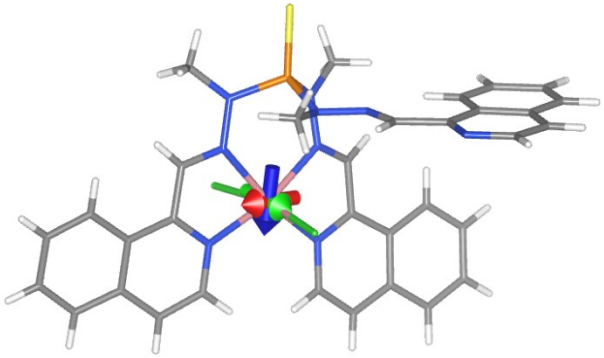
4

Orbital	Energy (eV)	Energy (cm^{-1})	d_{z^2}	d_{xz}	d_{yz}	$d_{x^2-y^2}$	d_{xy}
1	0.000	0.0	-0.998193	0.007053	0.024970	-0.040535	0.035969
2	0.158	1277.7	0.006308	-0.429925	-0.009581	0.455574	0.779413
3	0.190	1529.3	0.058237	-0.039348	0.415010	-0.790466	0.444960
4	1.107	8926.2	-0.011019	-0.769176	0.463559	0.034071	-0.438405
5	1.189	9590.2	0.007573	0.471100	0.782409	0.405970	0.032123

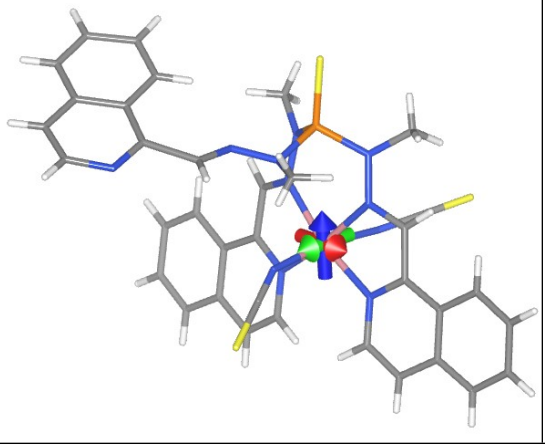
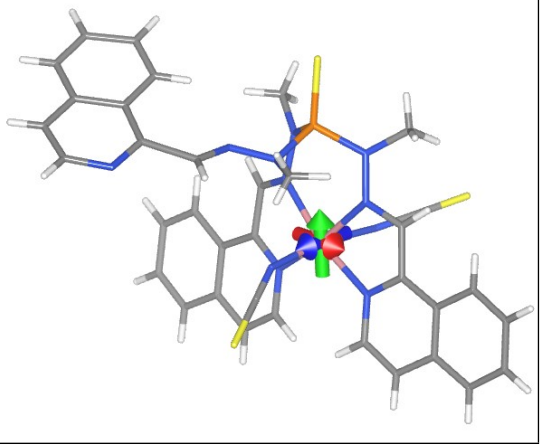
Compound 1



Compound **2**



Compound **3**

CASSCF	CASSCF/NEVPT2
	

Compound **4**

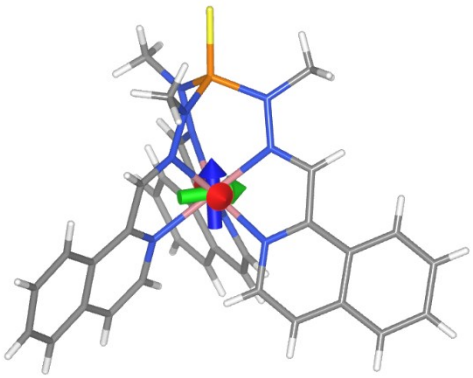


Figure S9.- Orientation of the *D*-tensor components in compounds **1**, **2**, **3** and **4**, obtained from CASSCF/NEVPT2 calculations. The reference axis *x*, *y* and *z* of the *D*-tensor are displayed in red, green and blue, respectively. Solvent molecules and counterions are omitted for clarity.

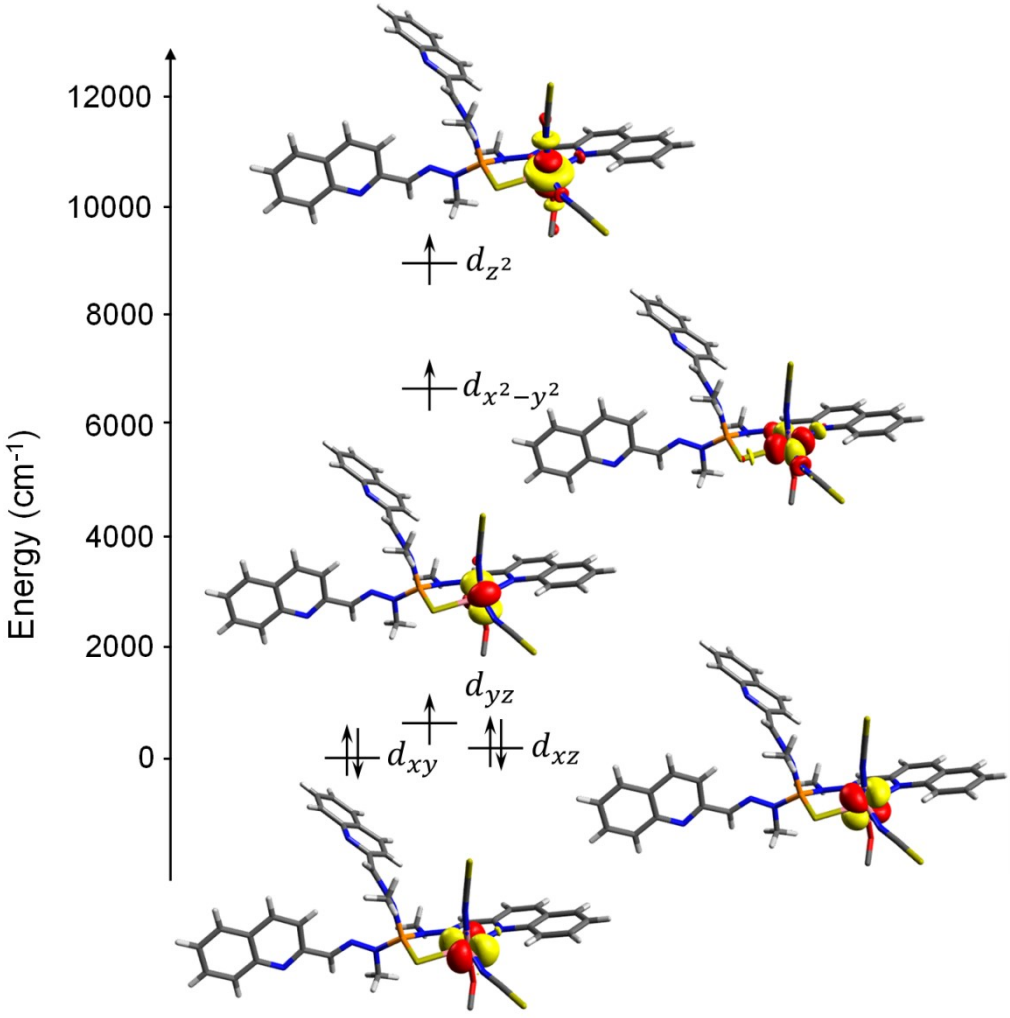


Figure S10.- NEVPT2-AILFT computed d-orbital energy diagram of **1**. Solvent molecules are omitted for clarity.

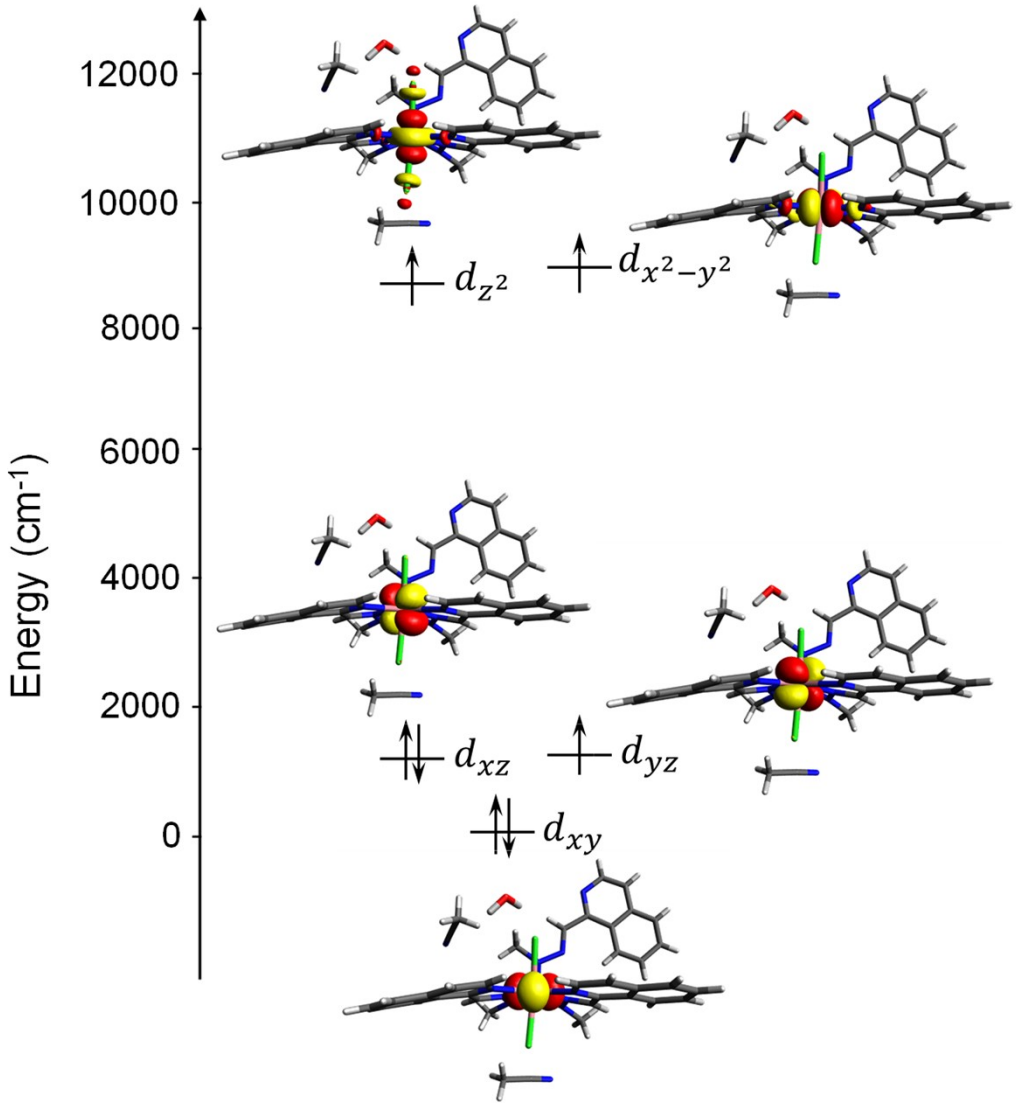


Figure S11. NEVPT2-AILFT computed d-orbital energy diagram of **2**.

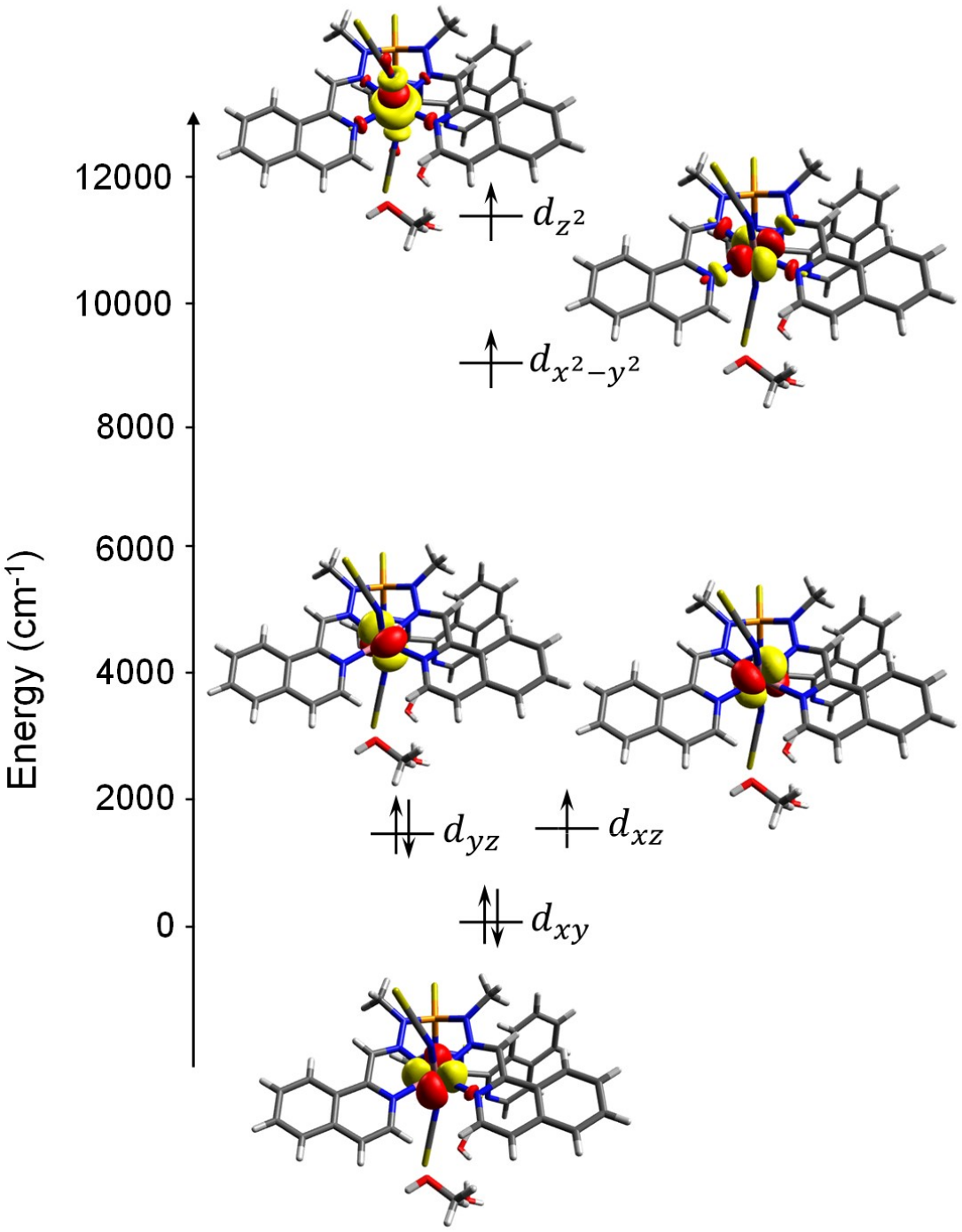


Figure S12. NEVPT2-AILFT computed d-orbital energy diagram of **3**.

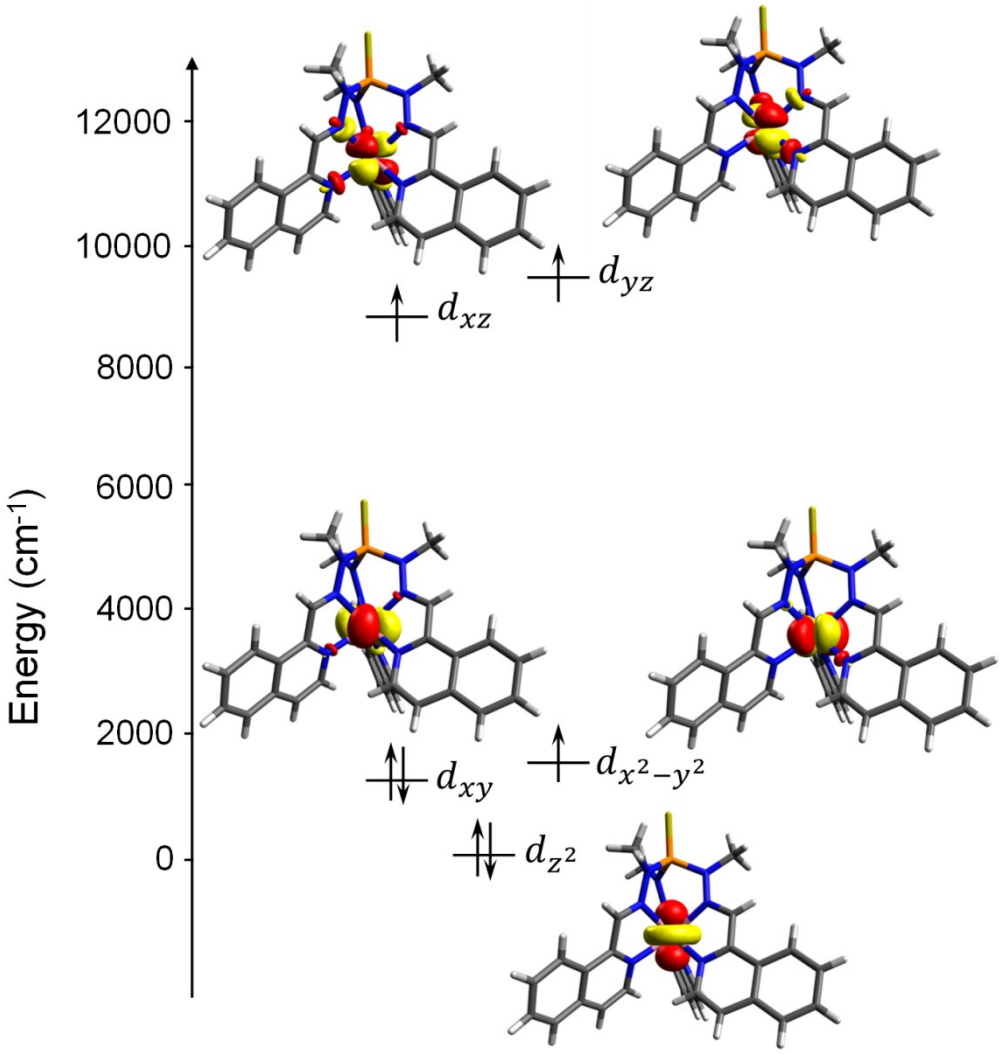


Figure S13. NEVPT2-AILFT computed d-orbital energy diagram of **4**. Counterions and solvent molecules are omitted for clarity.

Table S10. Contributions to *D*-tensor from CASSCF/NEVPT2 calculations for compounds **1**, **2** and **4**.

	1		**2**	
	D	*E*	*D*	*E*
$^4\Phi_1$	44.569	43.060	18.439	18.386
$^4\Phi_2$	35.115	-33.003	17.581	-17.591
$^4\Phi_3$	0.589	0.440	-13.042	0.007
$^4\Phi_4$	-7.594	0.542	0.439	0.451
$^4\Phi_5$	1.588	-3.431	3.719	3.812

4	
D	*E*
-139.557	0.000
5.685	-5.669
2.914	-3.726
4.189	5.066
0.503	0.103

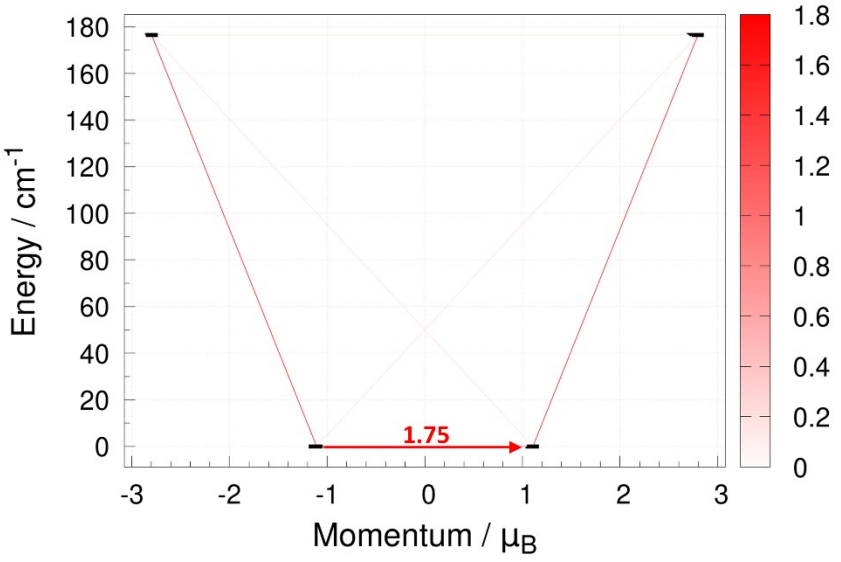


Figure S14. Possible relaxation pathways for complex **1**. The black lines indicate the KDs as a function of the magnetic moments. Red lines denote QTM in the ground state.

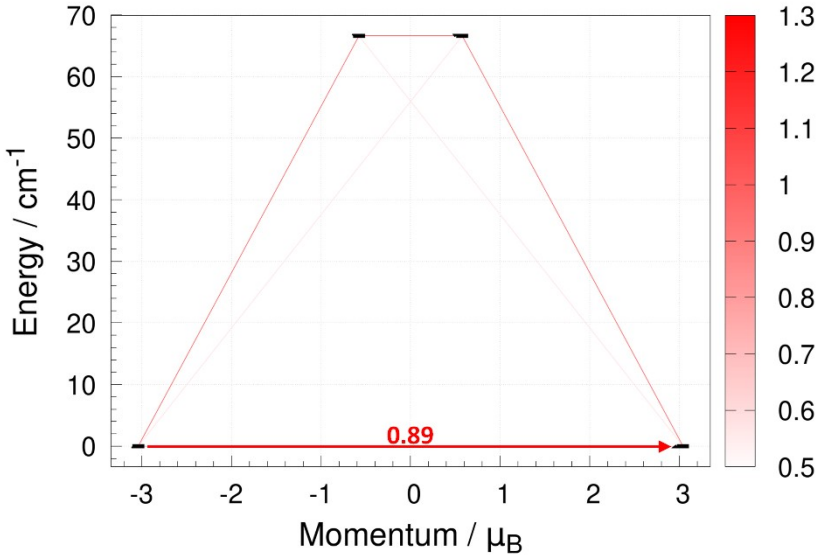


Figure S15. Possible relaxation pathways for complex **2**. The black lines indicate the KDs as a function of the magnetic moments. Red lines denote QTM in the ground state.

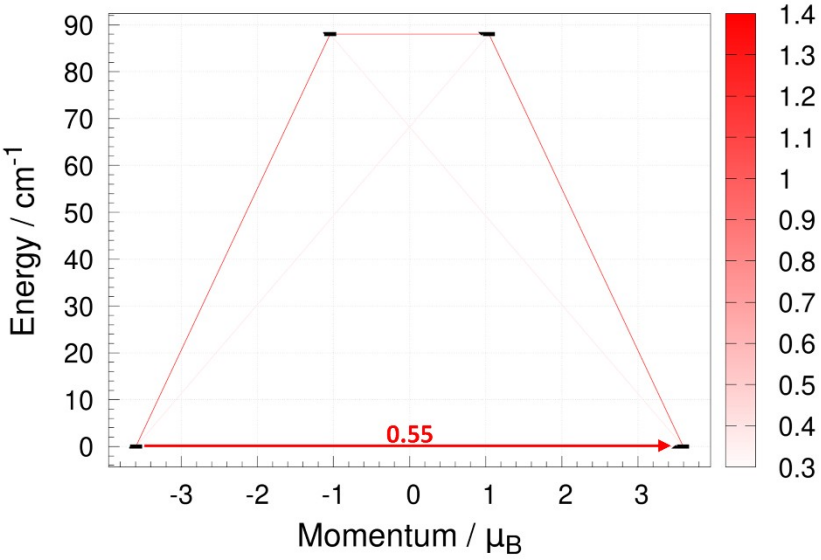


Figure S16. Possible relaxation pathways for complex **3**. The black lines indicate the KDs as a function of the magnetic moments. Red lines denote QTM in the ground state.

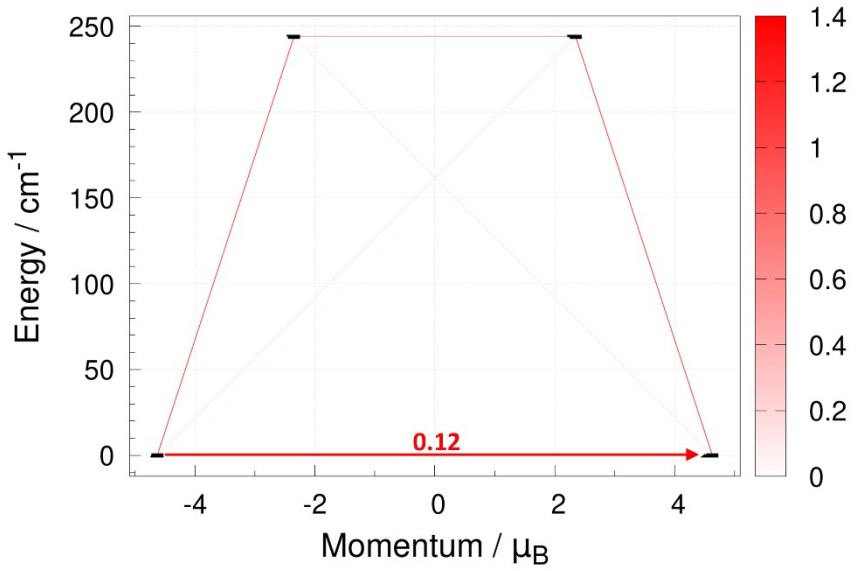


Figure S17. Possible relaxation pathways for complex **4**. The black lines indicate the KDs as a function of the magnetic moments. Red lines denote QTM in the ground state.

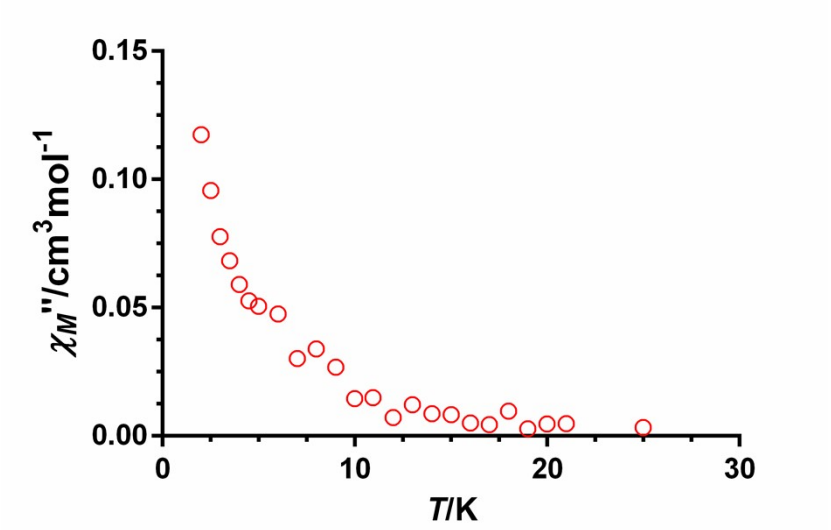


Figure S18.- Temperature dependence of the χ_M" at 10000 Hz for compound **4**.

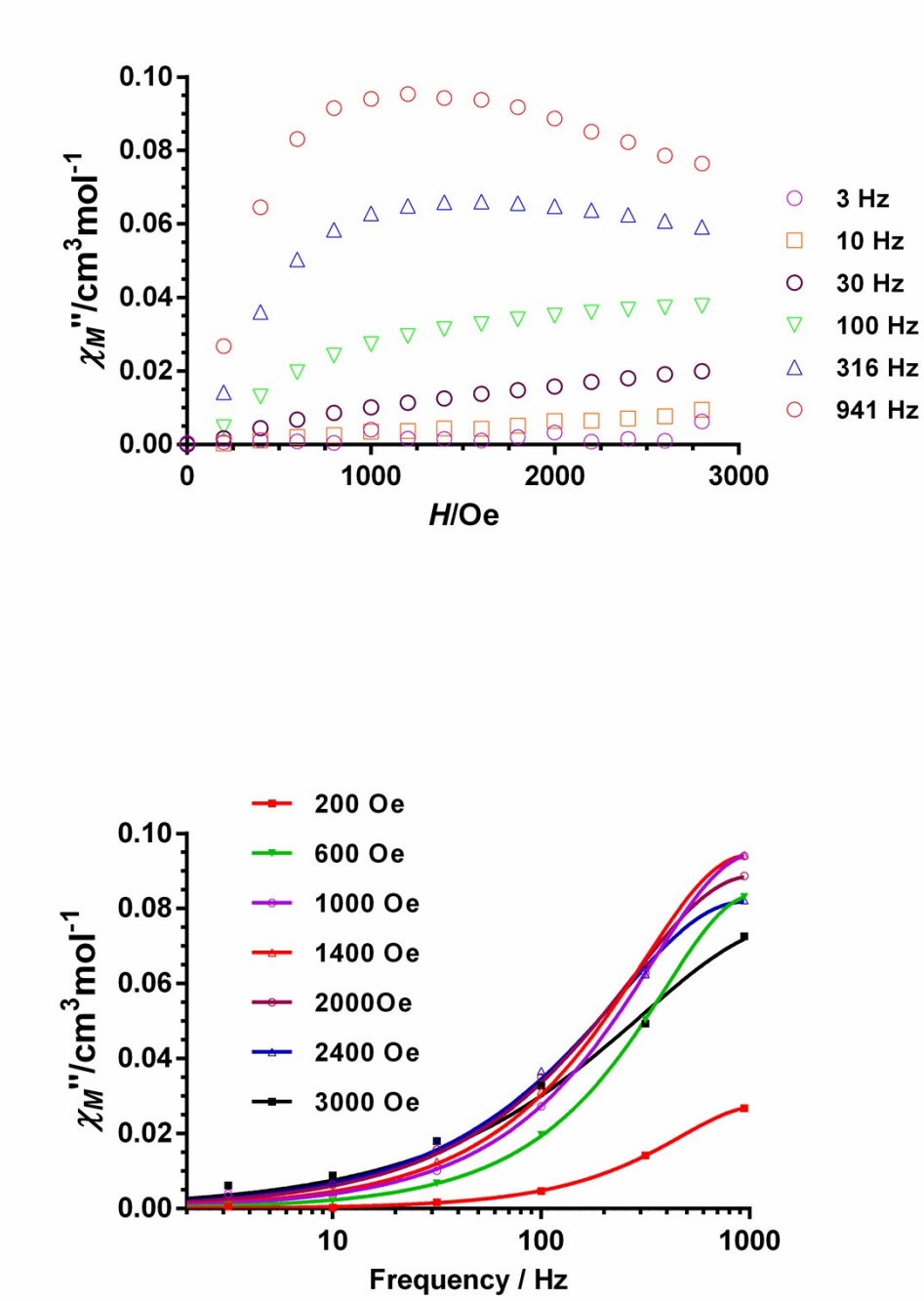


Figure S19.- Field dependence (top) and frequency dependence (bottom) of the of the out-of-phase signals for **2** at 2 K at the indicated frequencies and magnetic fields.

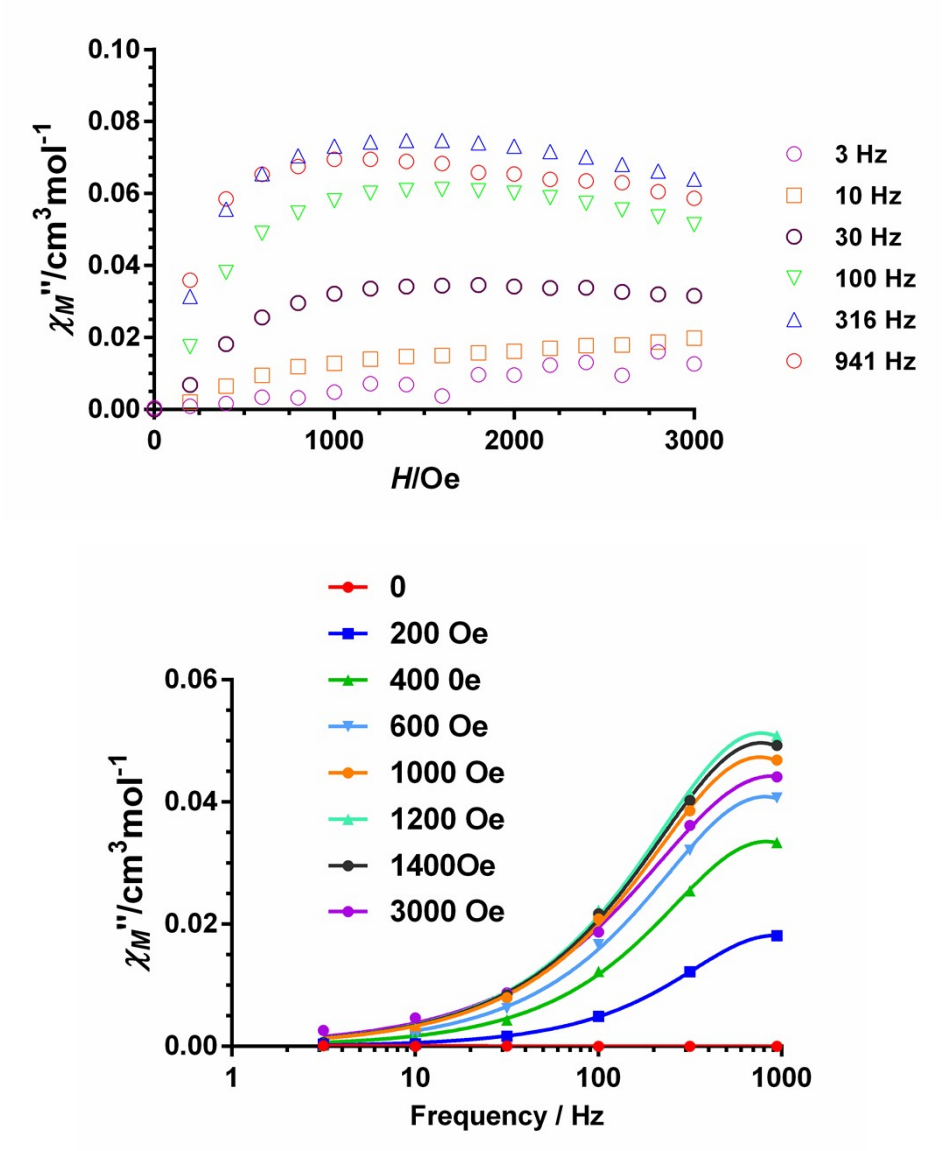


Figure S20.- Field dependence (top) and frequency dependence (bottom) of the of the out-of-phase signals for **3** at 2 K at the indicated frequencies and magnetic fields.

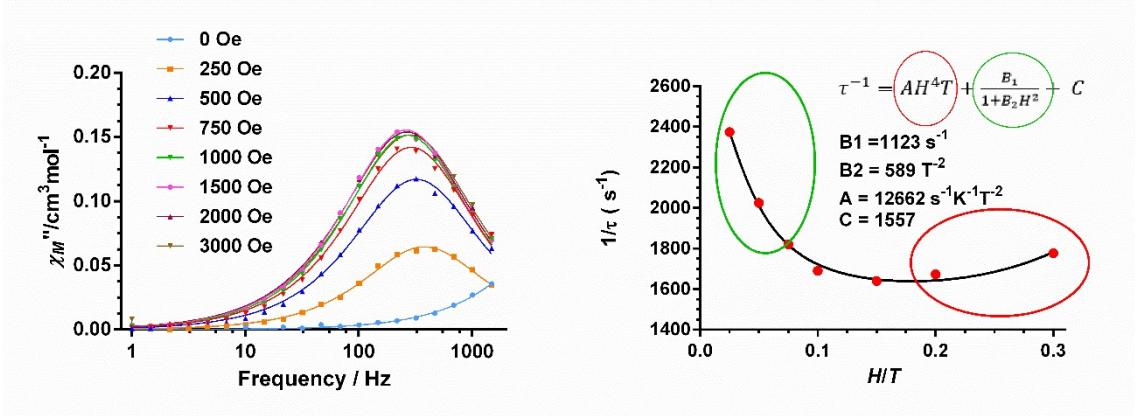


Figure S21.- Frequency dependence of χ_M" at the indicated magnetic fields for **4**. Solid lines represent the best fit to the generalized Debye model (left). Field dependence of the inverse of the relaxation times. The black solid line corresponds to the best fit to the equation and with the parameters indicated in the inset (right).

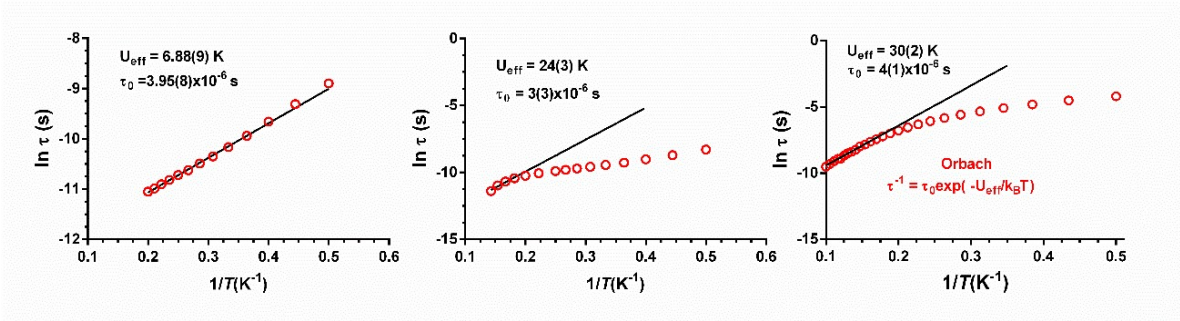


Figure S22.- Arrhenius plots for compounds **2** (left), **3** (centre) and **4** (right).

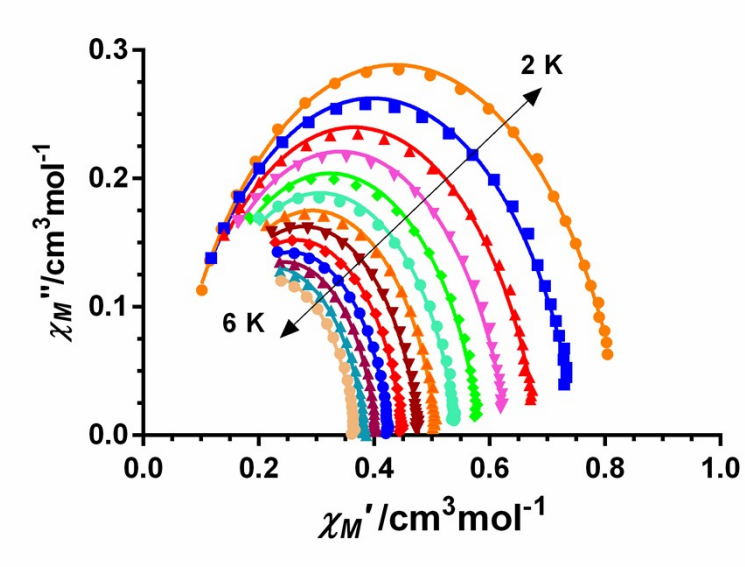


Figure S23. Cole-Cole plot for compound **2** at the indicated temperature range under a magnetic field of 0.12 T.

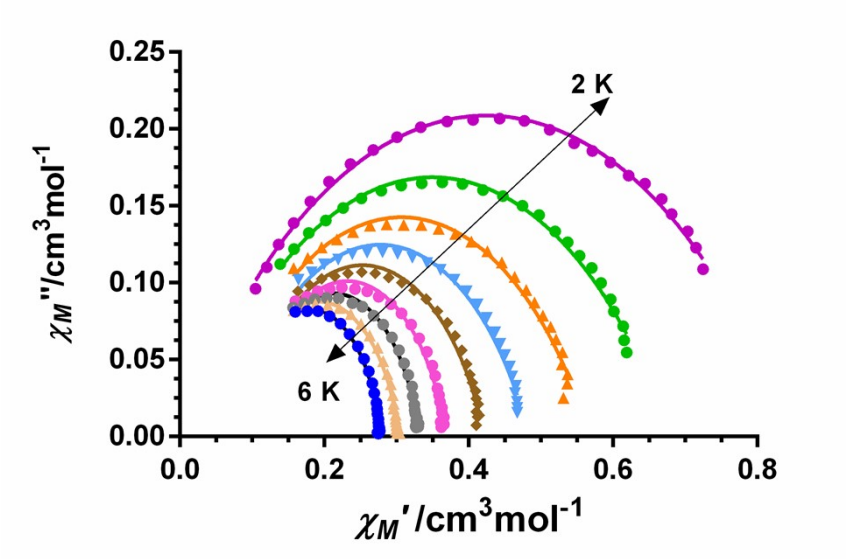


Figure S24. Cole-Cole plot for compound **3** at the indicated temperature range and under a magnetic field of 0.12 T.

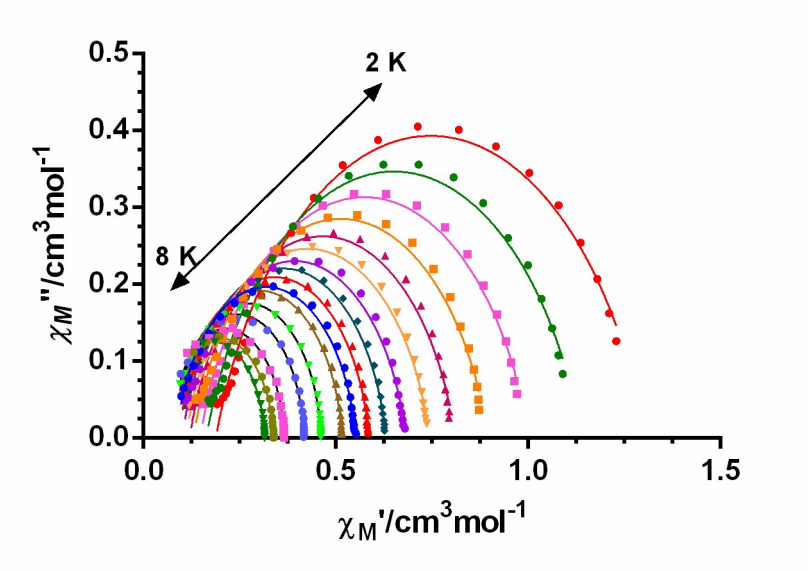


Figure S25. Cole-Cole plot for compound **4** at the indicated temperature range and under a magnetic field of 0.15 T.

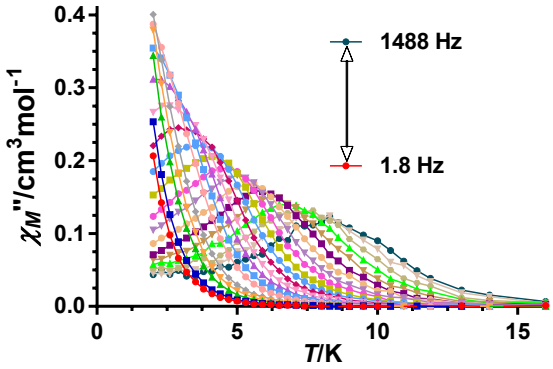


Figure S26.- Temperature dependence of the χ_M" at different frequencies under a magnetic field of 0.15 T for compound **4**.

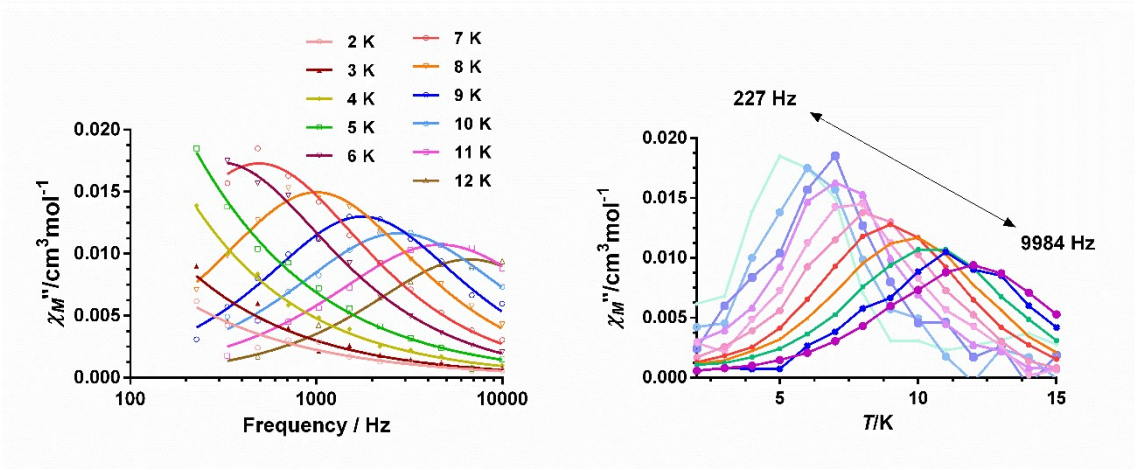


Figure S27.- Frequency dependence of the χ_M" at the indicated temperatures (left) and temperature dependence of the χ_M" at the indicated frequencies (right) for **4'**. Solid lines in the left panel represent the best fit to the generalized Debye model.