Electronic Supplementary Information

What Controls the Sign and Magnitude of Magnetic Anisotropy in Tetrahedral Co(II) Single-ion Magnets?

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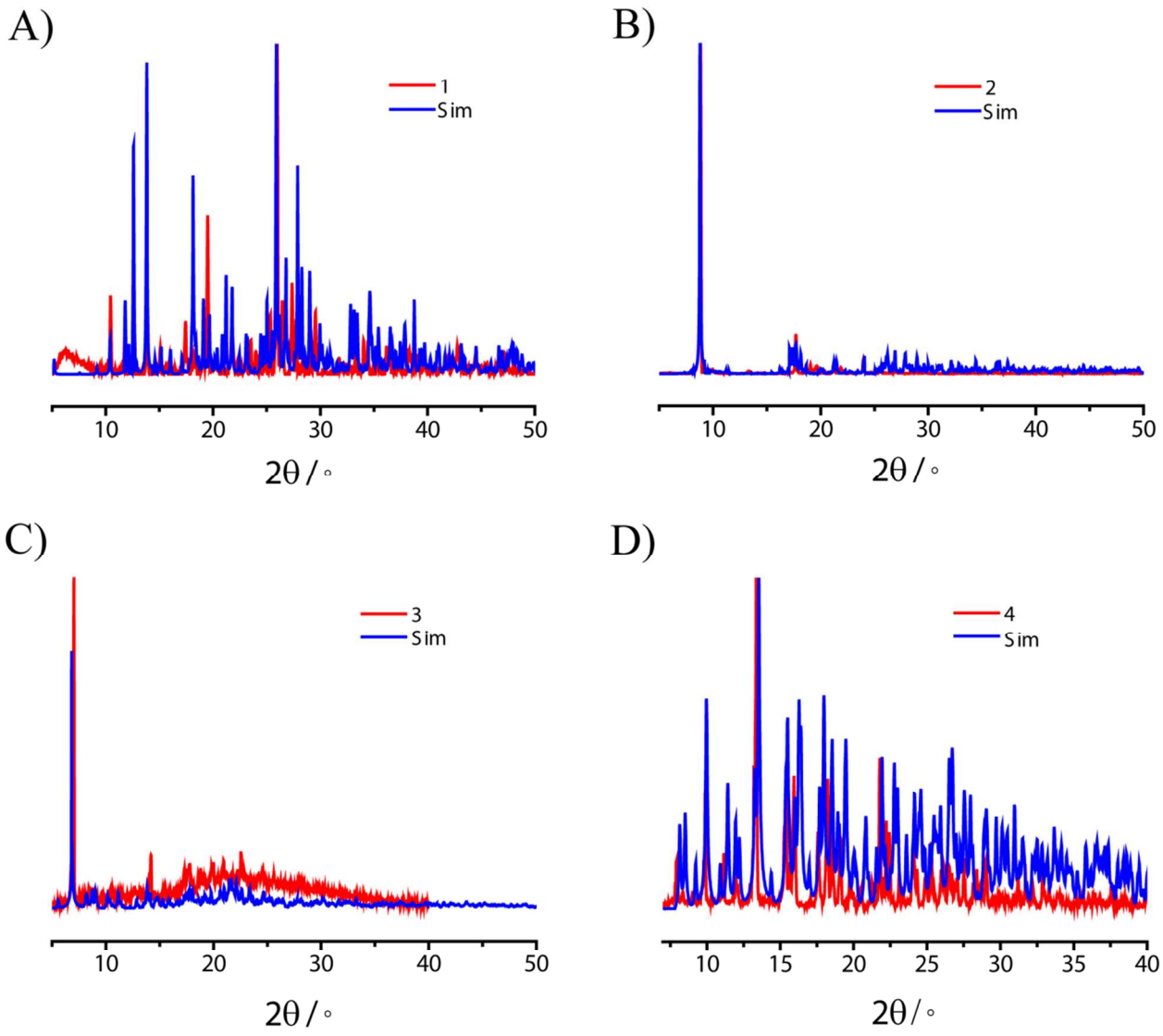

Figure S1. Overlay of experimental powder XRD and generated powder XRD for complexes A) **1**, B) **2** C) **3** and D) **4**.

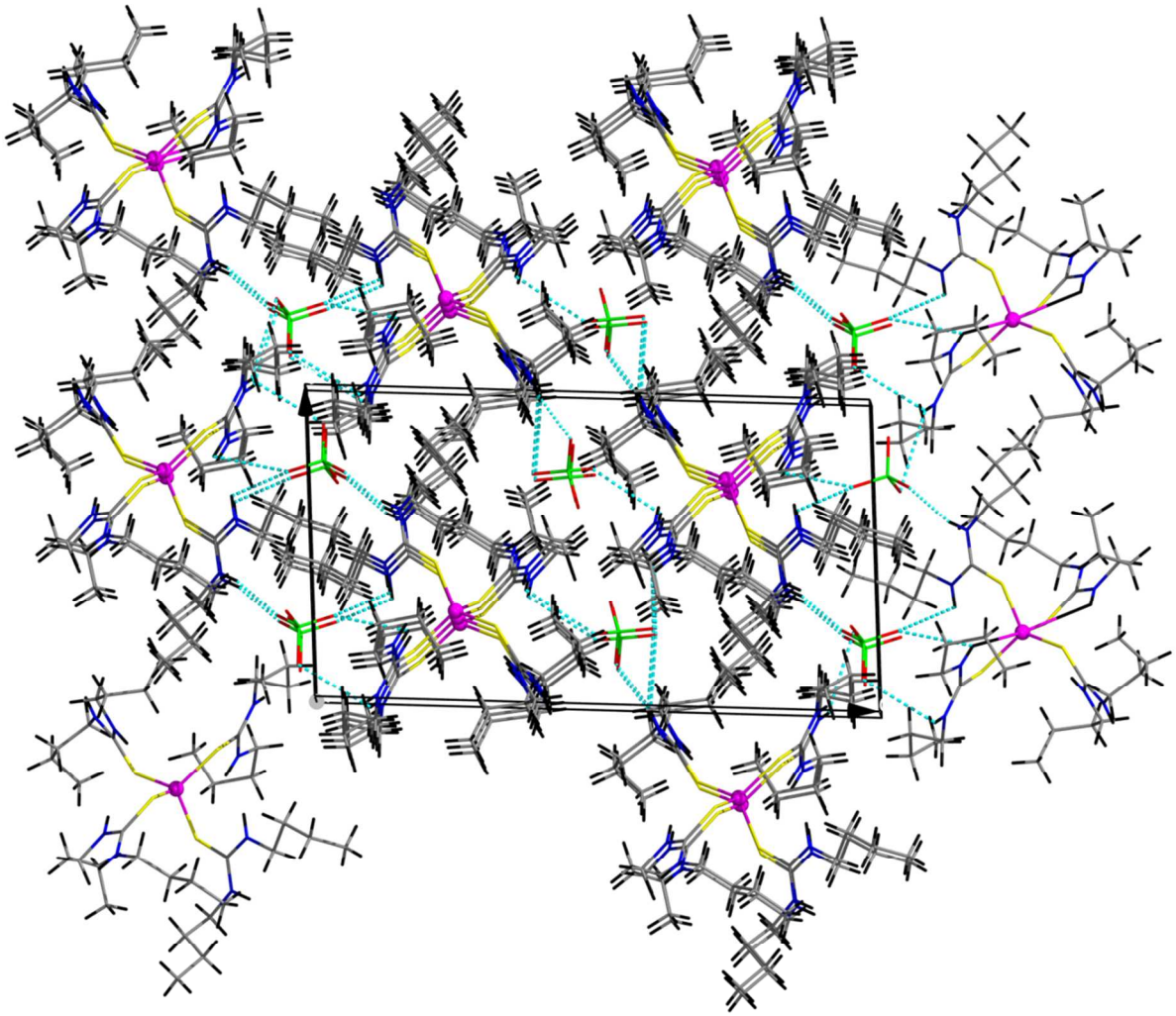

Figure S2. Packing diagram of **2**. Dotted sky blue bonds represent the H-bonding network in complex **2**.

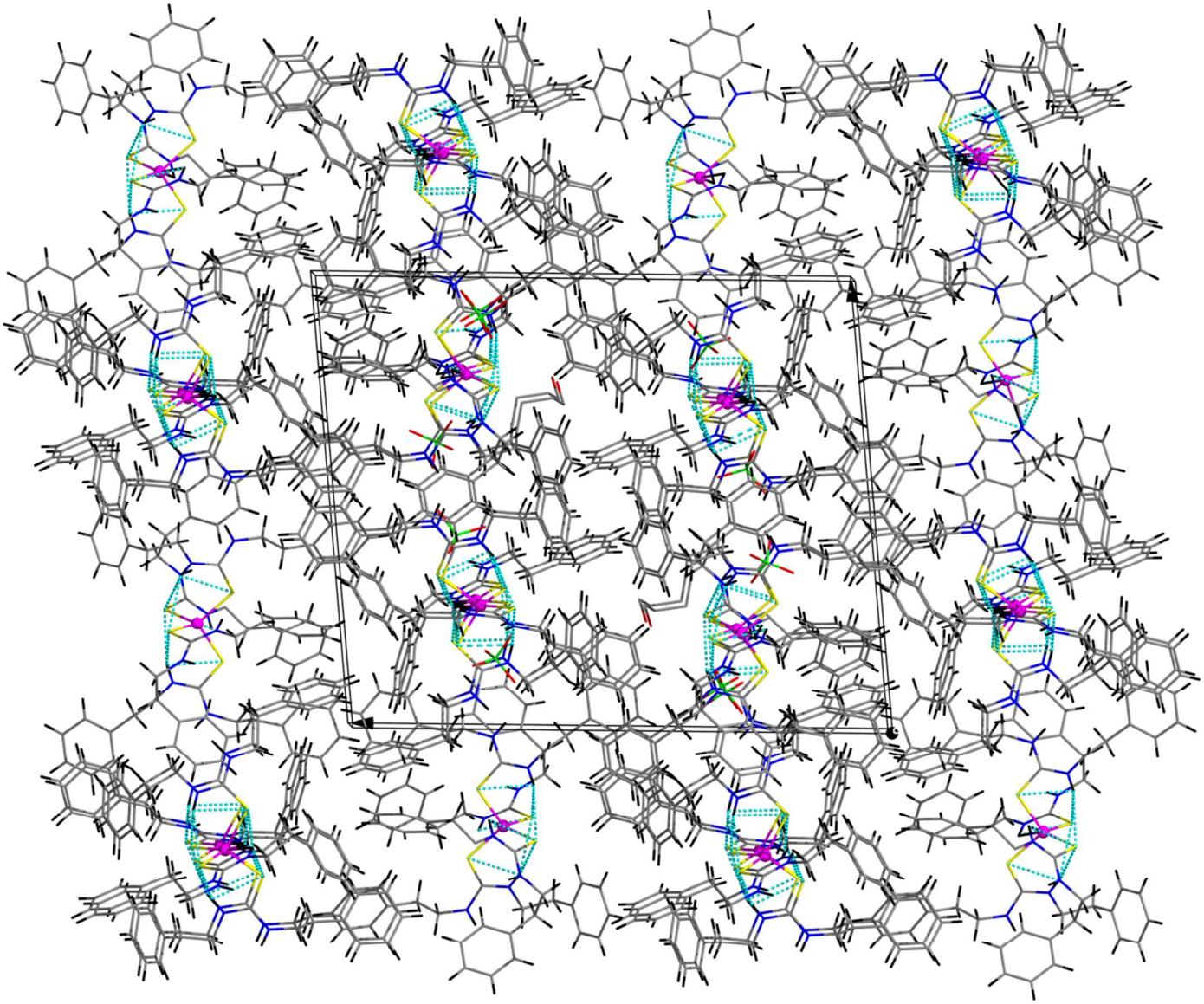

Figure S3. Packing diagram of **3**. Dotted sky blue bonds represents the H-bonding network in complex **3**.

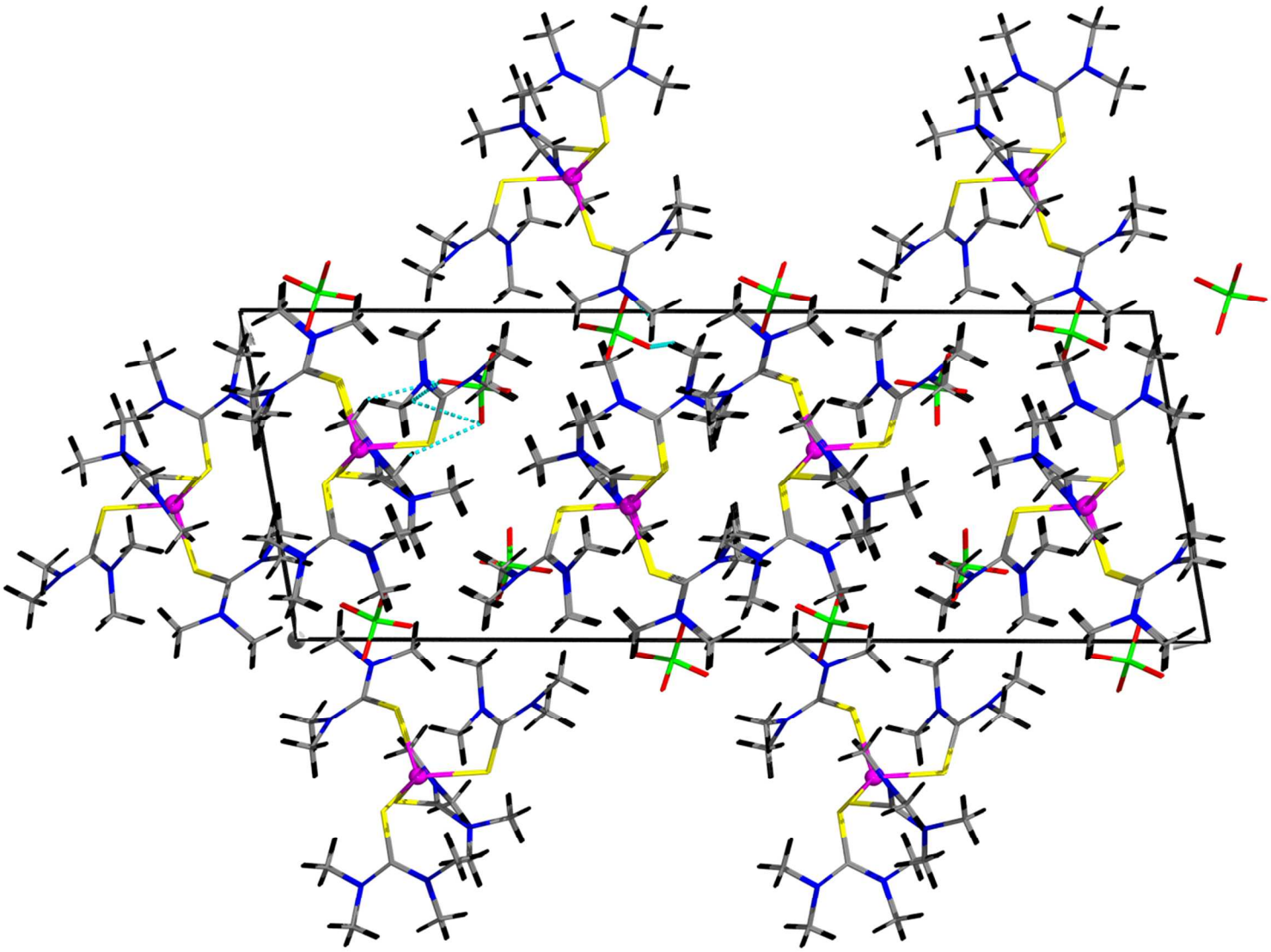

Figure S4. Packing diagram of **4**. Dotted sky blue bonds represents the H-bonding network in complex **4**.

Table S1. Atoms involved in inter and intramolecular hydrogen bonding and its corresponding bond distance and bond angles in complex **1.**

H-Bond Donor(D)-Acceptor(A)	D….A (Å)	∠DHA (°)
N12-H12B…O113_$1	2.985	137.81
N31-H31A…O101_$1	3.304	144.70
N51-H51A…O103_$1	3.003	156.03
N52-H52A…O103_$1	3.238	143.08
N52-H52A…O101_$1	3.030	161.56
N31-H31B…S11_$1	3.635	130.43
N52-H52A…N101_$1	3.567	170.57
N32-H32A…O92_$2	2.836	171.60
N31-H31A…O91_$2	3.020	123.85
N11-H11B…S31_$2	3.659	166.50
N51-H51B…S71_$2	3.570	146.86
O141-H14A…S61_$2	3.486	120.48
N41-H41A…O91_$3	2.964	166.15
N42-H42A…O93_$3	2.896	165.72
N81-H81B…S61_$3	3.586	164.53
N21-H21A…O112_$4	2.803	179.64
N22-H22A…O123_$4	2.914	116.59
N22-H22A…O111_$4	3.079	167.51
N72-H72A…O122_$5	2.866	155.29
N71-H71A…O122_$5	3.189	138.78
N71-H71A…O121_$5	3.021	164.77
N71-H71A…N121_$5	3.499	167.09
N62-H62A…O102_$6	2.946	165.88
O1-H1A…O102_$6	2.789	157.84
O1-H1B…O93_$6	3.011	130.85
O1-H1B…S51_$6	3.418	125.84
N82-H82A…O112_$7	2.802	170.79
N81-H81A…O113_$7	2.979	176.51
N82-H82B…O123_$8	3.193	131.08
N82-H82B…O121_$8	3.138	128.74
N61-H61B…O103_$9	2.891	158.37
N61-H61B…O102_$9	3.208	137.60
N61-H61B…N101_$9	3.454	157.93
N32-H32B…S41	3.720	142.34
N41-H41B…S21	3.433	165.05
N21-H21B…S11	3.759	153.64
N72-H72B…S81	3.718	161.69
N62-H62B…S81	3.854	159.27
N11-H11A…O123	3.066	161.92
N11-H11A…O111	3.094	113.96
N12-H12A…O122	2.842	167.13
N52-H52B…O93	3.174	168.01
N52-H52B…O92	2.925	122.17
N42-H42B… O102	3.026	114.65
N61-H61A…O1	2.918	164.84

Symmetry operators for generating equivalent atoms: $1 x, -y, z+1/2; $2 x, -y, z-1/2; $3 x, -y+1, z-1/2; $4 x, y+1, z; $5 x+1, y, z; $6 x, -y+1, z+1/2; $7 x+1, y+1, z+1; $8 x+1, -y, z+1/2; $9 x, y, z+1

Table S2. Atoms involved in inter and intramolecular hydrogen bonding and its corresponding bond distance and bond angles in complex **2**

H-Bond Donor(D)-Acceptor(A)	D….A (Å)	∠DHA (°)
N22-H22A …O54_$1	2.989	166.14
N32-H32A …O53_$2	2.916	152.11
N42-H42A …O64_$3	2.940	154.12
N11-H11A …O62	2.828	146.72
N12-H12A …S41	3.544	166.06
N21-H21A …S31	3.484	165.23
N31-H31A…S21	3.501	163.29
N41-H41A…S11	3.617	164.40

Symmetry operators for generating equivalent atoms: $1 -x+1, -y+1,-z+1; $2 -x+1,-y,-z+1; $3 x, y-1, z

Table S3. Atoms involved in inter and intramolecular hydrogen bonding and its corresponding bond distance and bond angles in complex **3**

H-Bond Donor(D)-Acceptor(A)	D….A (Å)	∠DHA (°)
N(71)-H(71A_b)… O171_$1	3.039	131.77
N(92)-H(92)… O192_a_$2	3.074	155.26
N(92)-H(92)… O19B_b_$2	3.148	155.27
N(11)-H(11)…S31	3.540	158.73
N(12)-H(12)…O174	3.000	154.61
N(31)-H(31)…S11	3.533	157.34
N(32)-H(32)…O204	2.883	147.99
N(51)-H(51)…O191_a	2.848	154.26
N(51)-H(51)… O19A_b	2.872	149.85
N(52)-H(52)…S71	3.425	169.17
N(72)-H(72)…S51	3.517	134.79
N(71)-H(71A_a)… O182_a	2.691	148.16
N(71)-H(71A_b)… O2A_b	3.116	135.38
N(91)-H(91)…S151	3.589	155.41
N(112)-H(112)…S131	3.419	157.19
N(131)-H(131)…S111	3.508	149.30
N(132)-H(132)…O171	2.866	147.36
N(151)-H(151)…S91	3.472	155.38
N(152)-H(152)… O181_a	2.948	165.85
N(152)-H(152)… O1A_b	3.193	168.88

Symmetry operators for generating equivalent atoms: $1 x+1, y, z; $2 x-1, y+1, z; $3 x-1, -y+1, z

Table S4. Atoms involved in inter and intramolecular hydrogen bonding and its corresponding bond distance and bond angles in complex **4**

Intermolecular hydrogen bonding

H-Bond Donor(D)-Acceptor(A)	D….A (Å)	∠DHA (°)
C44-H44A...O53_$1	3.355	131.9
C13-H13C...O54_$2	3.274	147.1
C32-H32B...O63_$3	3.304	134.8
C33-H33C...O64_$3	3.476	146.7
C25-H25B...O63_$4	3.575	175.8
C25-H25B...O64_$4	3.300	128.0
C23-H23B…O52_$5	3.437	166.18
C23-H23C…O63_$6	3.586	172.02
C24-H24B…O51_$7	3.392	141.39
C44-H44C…O53_$1	3.304	127.01
C45-H45B…O54_$8	3.484	170.33
C45-H45C…S41_$1	3.890	160.78
C15-H15B…O53	3.164	119.98
C34-H34B…O64	3.455	152.83
C42-H42C…O61	3.178	119.47
C43-H43B…O61	3.378	151.87
C25-H25C…S11	3.425	125.43
C35-H35C…S21	3.559	132.72
C45-H45A…S31	3.792	156.23

Symmetry operators for generating equivalent atoms: $1= -x+1, -y, -z+1; $2= -x+2, -y+1, -z+1; $3= -x+1, y+1/2, -z+3/2; $4= -x+1, y-1/2, -z+3/2; $5= x, -y+1/2, z+1/2; $6= x+1, y, z; $7= -x+2, -y, -z+1; $8= x-1, y, z

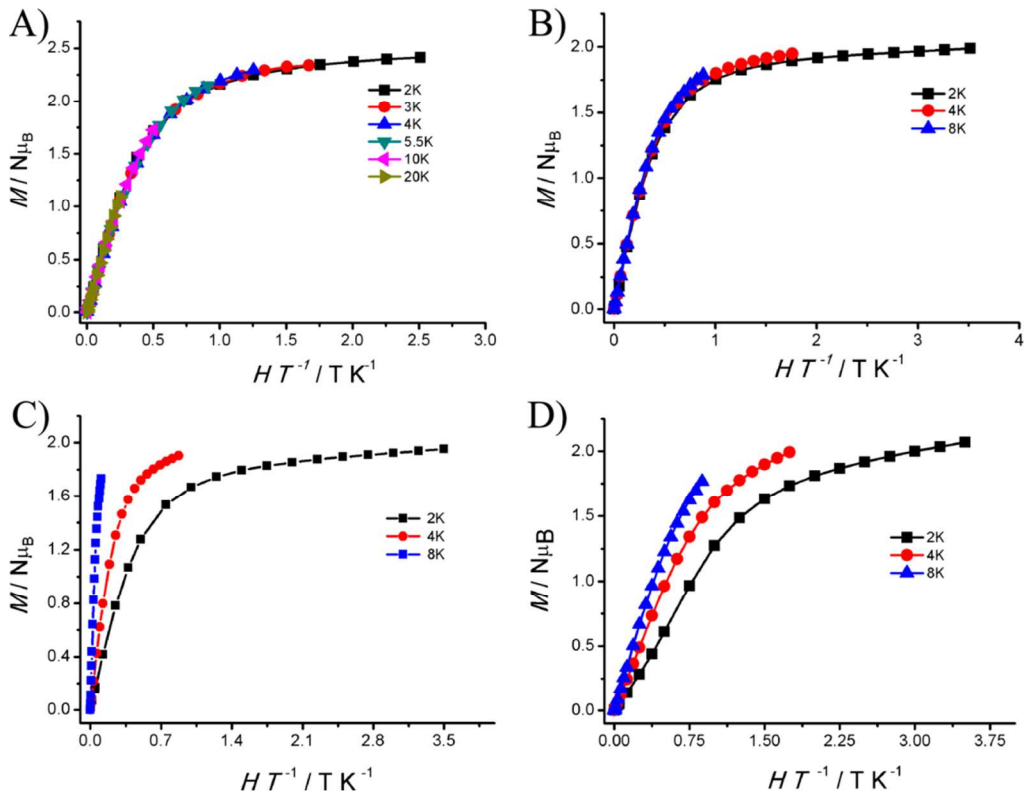

Figure S5. A-D) Reduced magnetization plot for complexes **1-4** respectively.

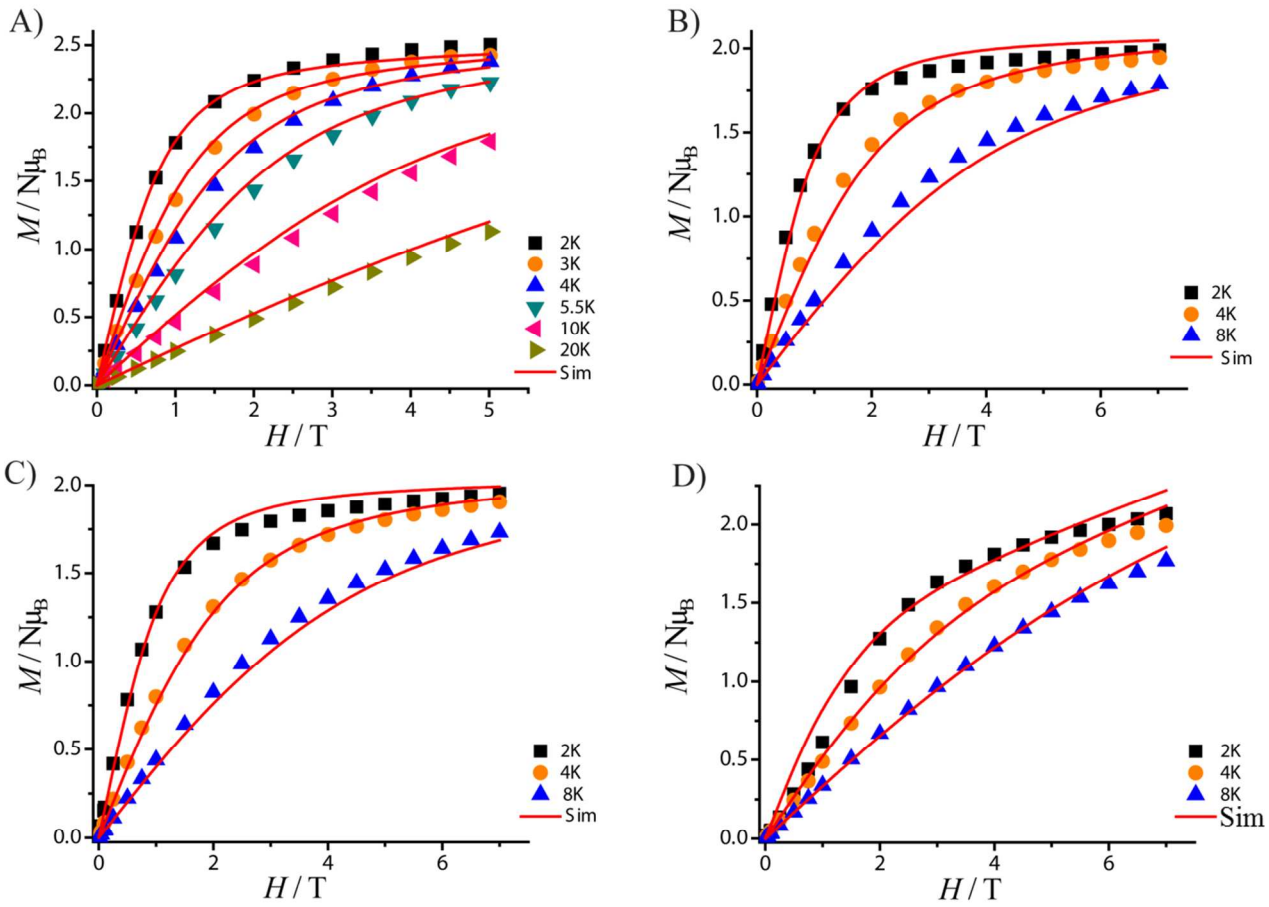

Figure S6. A-D) Field dependent magnetization data collected on polycrystalline sample of complexes **1**-**4** respectively. The red line represents the simulation obtained by taking magnetic anisotropy as negative.

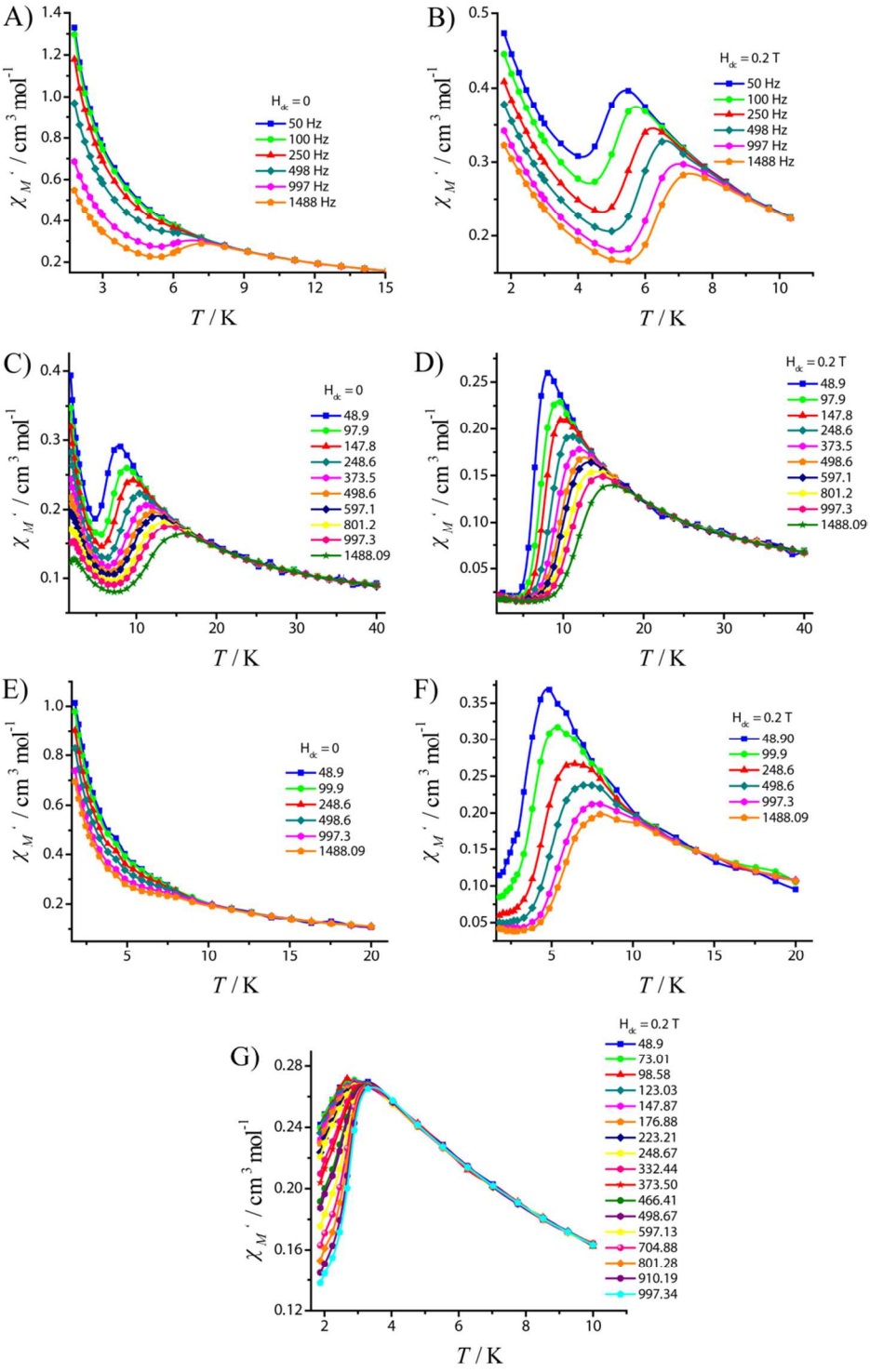

Figure S7. Frequency dependent in-phase susceptibility signals for complexes **1-3** in zero dc field (panels A, C and E) respectively and in the presence of 0.2 Tesla of dc bias field for complexes **1-4** (panels B, D, F and G) respectively.

Table S5. Fitting parameters for Cole-Cole plot of **1**.

S.No.	Temp (K)	χ_S	χ_T	τ	α	residual
1	1.8	0.141800	1.15578	0.256378E-03	0.112938	0.513441E-02
2	2.0	0.127916	1.02621	0.247103E-03	0.112600	0.379937E-02
3	2.2	0.119084	0.934292	0.241150E-03	0.111852	0.306346E-02
4	2.4	0.111090	0.842886	0.235896E-03	0.109727	0.247141E-02
5	2.6	0.103694	0.770729	0.230711E-03	0.108879	0.197318E-02
6	2.8	0.101059	0.710621	0.228597E-03	0.105198	0.212741E-02
7	3.0	0.0928849	0.659082	0.223553E-03	0.108352	0.146351E-02
8	3.2	0.0905895	0.615192	0.221282E-03	0.105340	0.132837E-02
9	3.4	0.0842011	0.576592	0.216165E-03	0.105778	0.115359E-02
10	3.6	0.0820646	0.542277	0.213399E-03	0.103400	0.905385E-03
11	4.0	0.0750875	0.485850	0.203469E-03	0.0977402	0.635469E-03
12	5.0	0.0744820	0.385816	0.152617E-03	0.0772965	0.350440E-03
13	6.0	0.0804064	0.320814	0.821952E-04	0.0485771	0.559532E-04
14	7.0	0.0876068	0.275200	0.331772E-04	0.0119805	0.165190E-04

Table S6. Crystallographic table for **5** and **6**.

	5	**6**
Formula	$Zn_1C_8H_{22}N_{12}O_6S_4$	$Zn_1C_{36}H_{80}N_8O_8S_4Cl_2$
Size [mm]	0.32 x 0.29 x 0.21	0.22 × 0.21 × 0.14
System	Orthorhombic	Triclinic
Space group	*Iba2*	*P-1*
a [Å]	18.721(8)	12.892(4)
b [Å]	10.223(4)	19.843(6)
c [Å]	12.798(5)	20.783(6)
α [°]	90	82.912(3)
β [°]	90	81.025(3)
γ [°]	90	89.725(2)
V [Å^3]	2449.3(17)	5210.9(3)
Z	4	2
ρ_{calcd}[g/cm^{-3}]	1.562	1.431
$2\Theta_{max}$	58.16	49.99
Radiation	Mo K_α	Mo K_α
λ [Å]	0.71073	0.71073
T [K]	100	100
Reflns	8447	81491
Ind. reflns	3236	18350
reflns with $I>2\sigma(I)$	2330	15970
R1	0.0556	0.0633
wR2	0.1072	0.1784

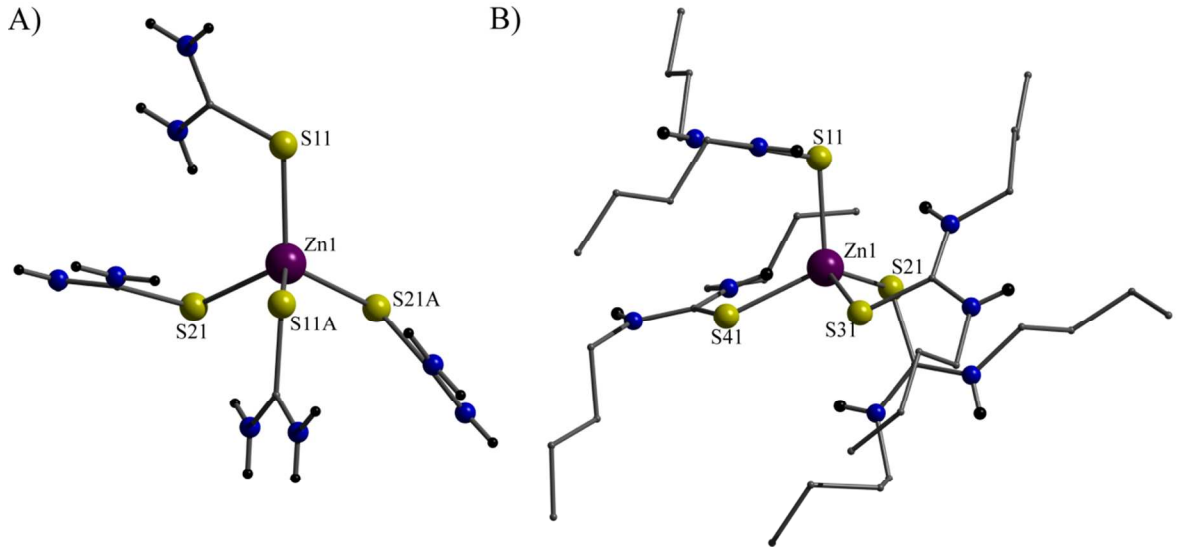

Figure S8. Ball and stick representation of crystal structures of A) **5** and B) **6**.

Table S7. Fitting parameters for Cole-Cole plot of **2**.

S.No.	T(K)	$\chi_{S,tot}$	$\Delta\chi_1$	τ_1	α_1	$\Delta\chi_2$	τ_2	α_2	residual
1	1.8	0.299776	0.323573	0.0128	0.466085	0.674726	0.380	0.166183	0.828420E-04
2	2.2	0.181069	0.345441	0.0056	0.551122	0.559615	0.364	0.168926	0.788954E-04
3	2.4	0.249406	0.201869	0.0114	0.376982	0.534281	0.357	0.165999	0.693386E-04
4	2.6	0.225327	0.215956	0.0133	0.420857	0.471414	0.344	0.142842	0.113516E-03
5	2.8	0.248056	0.177920	0.0256	0.339945	0.419801	0.319	0.114266	0.824624E-04
6	3.0	0.215845	0.192412	0.0203	0.373905	0.382002	0.268	0.0839967	0.157305E-03
7	3.2	0.213640	0.167928	0.0207	0.319821	0.359188	0.218	0.0617061	0.170578E-03
8	3.4	0.199997	0.168283	0.0197	0.303455	0.327731	0.169	0.0313561	0.144651E-03
9	3.6	0.179267	0.152048	0.0121	0.297267	0.327349	0.124	0.0287548	0.203042E-03
10	4.0	0.172336	0.123874	0.0108	0.195225	0.297730	0.0695	0.0113108	0.121089E-03
11	5.0	0.112574	0.0846565	0.0017	0.188102	0.283739	0.0159	0.0181964	0.169843E-03
12	6.0	0.0585294	0.0970530	0.00033	0.261736	0.251428	0.00512	0.0145644	0.219011E-03
13	7.0	0.0426688	0.0890793	0.000169	0.238456	0.221706	0.00209	0.0129184	0.241286E-03
14	8.0	0.0413012	0.0719046	0.000111	0.161904	0.200150	0.00101	0.00979929	0.175628E-03
15	10.0	0.0552286	0.0976594	0.000387	0.105890E-07	0.104577	0.00018	0.0508785	0.289514E-03
16	12.0	0.0163502	0.164124	0.000117	0.0240485	0.0385790	0.210750E-18	0.380652	0.171134E-03

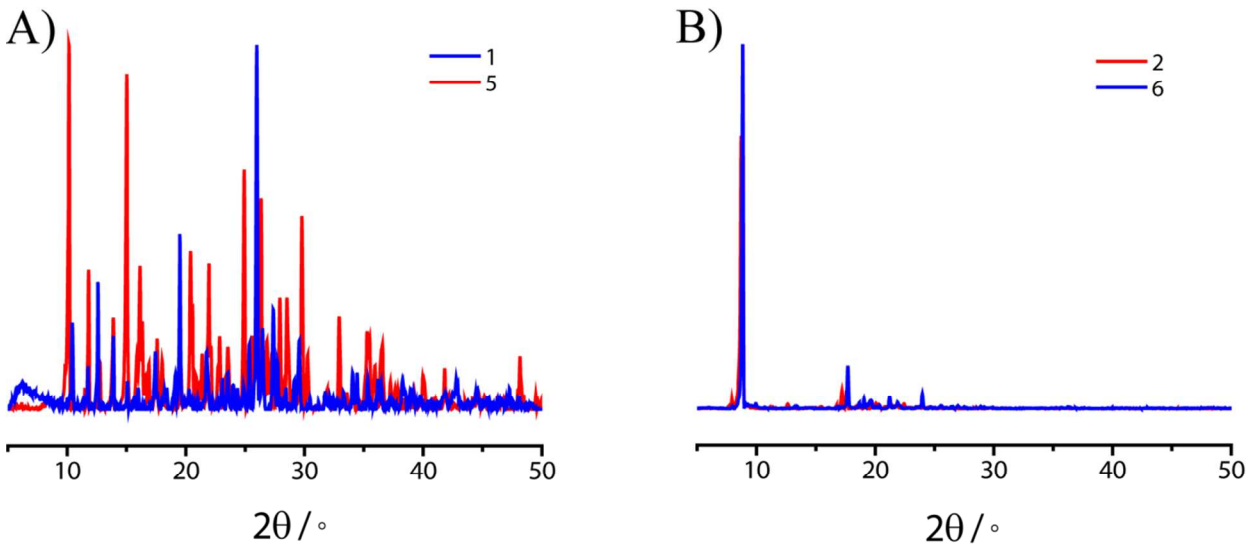

Figure S9. Powder XRD pattern of A) Complex **1** and its diamagnetic analogue prepared under the same condition as **1**. B) Complex **2** and Complex **6**.

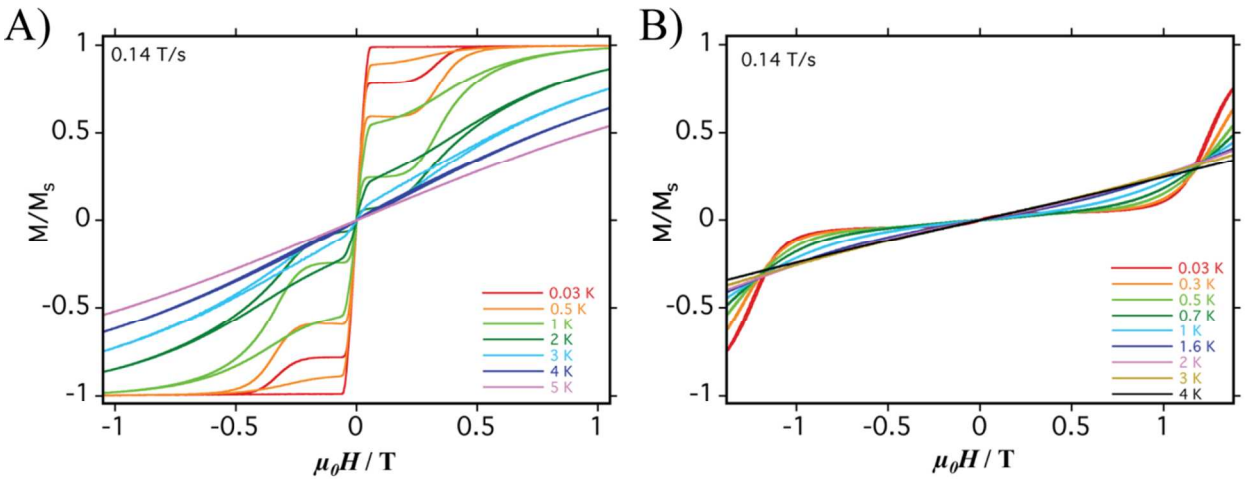

Figure S10. A and B) Temperature dependent hysteresis loop measurement performed on a single crystal of 100% sample of **3** and **4** respectively, where the external magnetic field is aligned parallel to the easy axis.

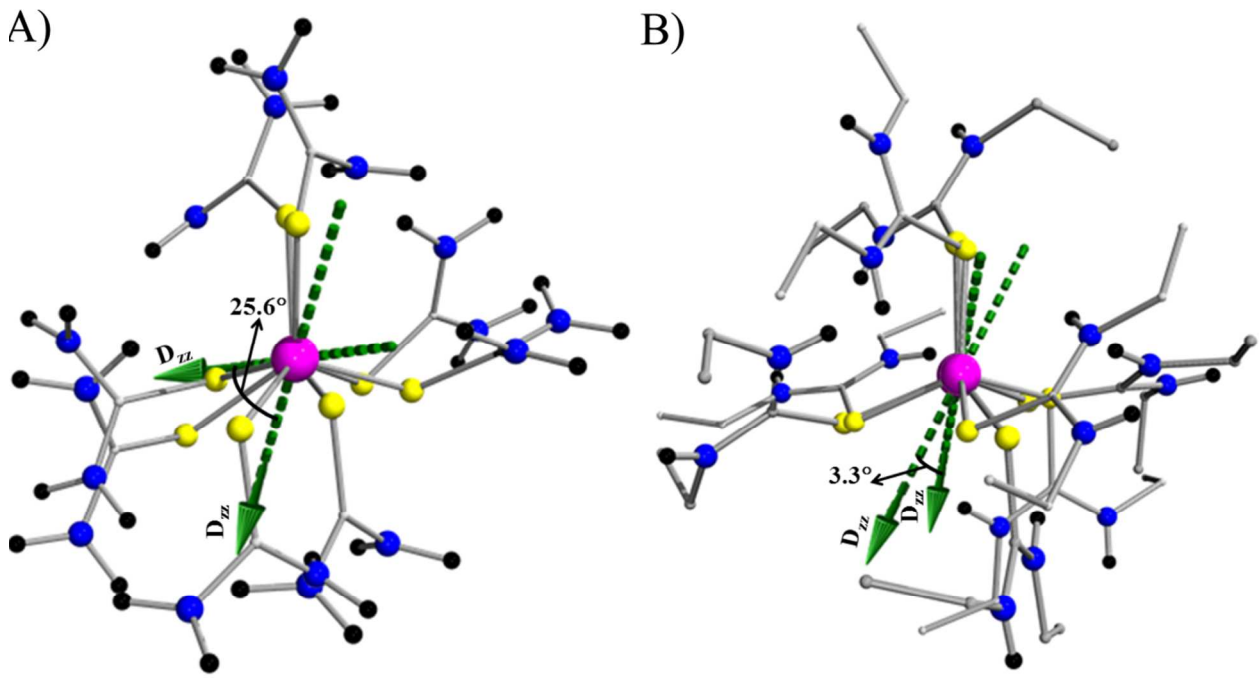

Figure S11. D_{zz} orientations between the crystallographically distinct molecules in A) Complex **1** and B) Complex **3**.

Table S8. D_{zz} orientation angle (°) with respect to the Co-sulphur bonds.

Label	**1**a(°)	**2**(°)	**4**(°)	Label	**1**b(°)	Label	**3**a(°)	Label	**3**b(°)
Co-S11	75.959	24.137	66.577	Co-S51	72.464	Co-S11	36.017	Co-S91	56.666
Co-S21	59.958	92.651	42.803	Co-S61	16.907	Co-S31	55.779	Co-S111	35.707
Co-S31	24.910	66.549	74.012	Co-S71	41.904	Co-S51	64.035	Co-S131	44.963
Co-S41	46.874	64.271	31.096	Co-S81	83.738	Co-S71	45.640	Co-S151	65.528

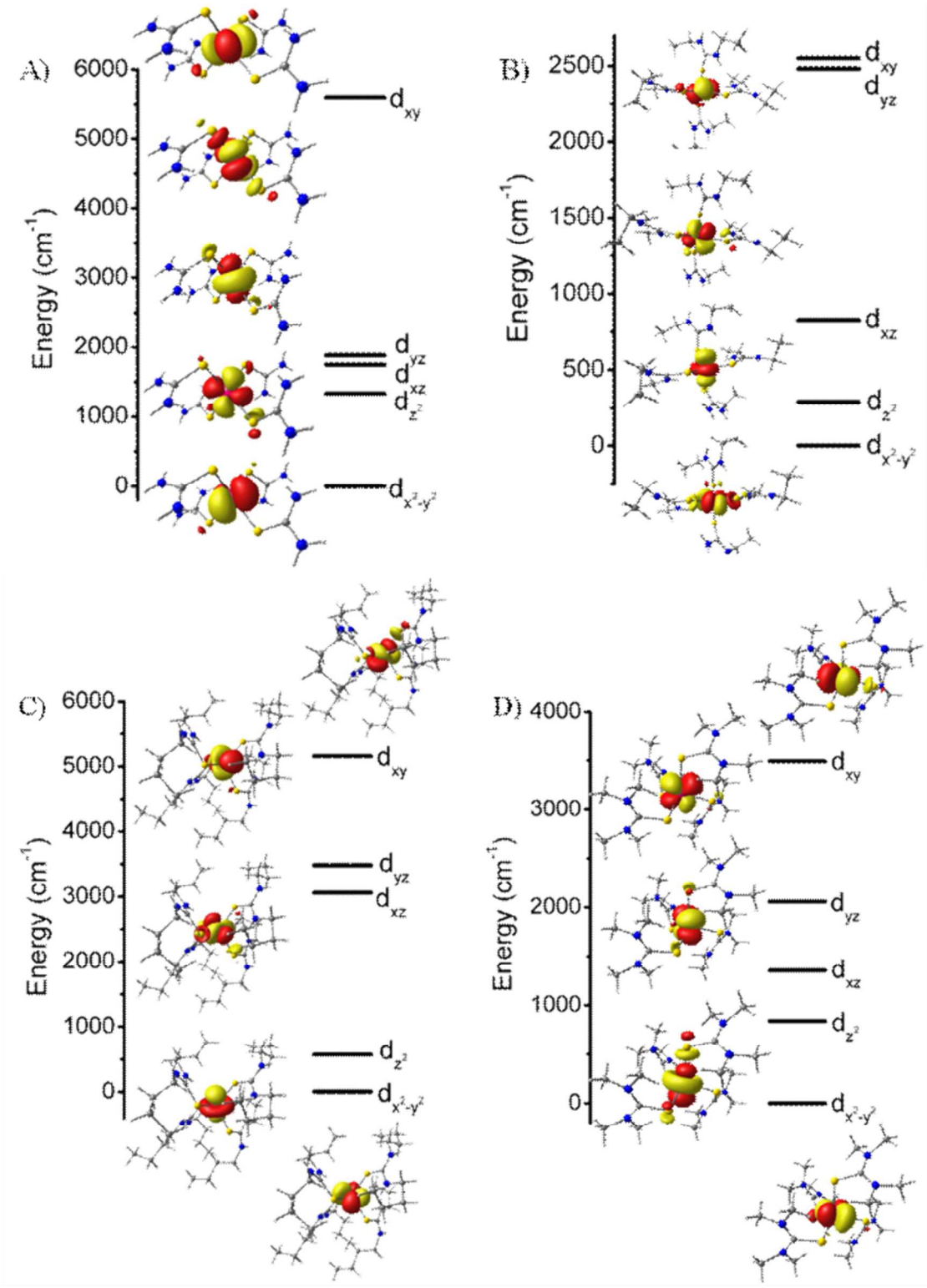

Figure S12. NEVPT2 computed d-orbital energy orderings for low-lying quartet state, $^4T_2(F)$ for complexes A-D) **1-4** respectively using ORCA [1] suite.

Table S9. The individual values for 2θ and ω parameters based on S4 symmetry in complexes **1**-**4**.

	1a	**1**b	**2**	**3**a	**3**b	**4**
S1-Co-S2	93.9	92.1	95.3	99.8	100.6	120.7
S3-Co-S4	89.2	90.0	96.0	99.1	97.9	109.3
X-Co-S1-C1	-12.9	-19.1	0.8	-8.0	-0.6	-8.0
X-Co-S2-C2	-25.3	19.5	-3.66	1.14	5.94	-74.5
X-Co-S3-C3	6.8	7.8	0.3	2.8	2.9	77.8
X-Co-S4-C4	8.8	-26.1	-4.7	9.4	-1.2	72.6

References:-

(1) (a) Neese, F., The ORCA program system. *Wires Comput Mol Sci.* **2012,** *2* (1), 73-78; (b) Neese, F.; Petrenko, T.; Ganyushin, D.; Olbrich, G., Advanced aspects of ab initio theoretical optical spectroscopy of transition metal complexes: Multiplets, spin-orbit coupling and resonance Raman intensities. *Coord. Chem. Rev.* **2007,** *251*, 288-327.